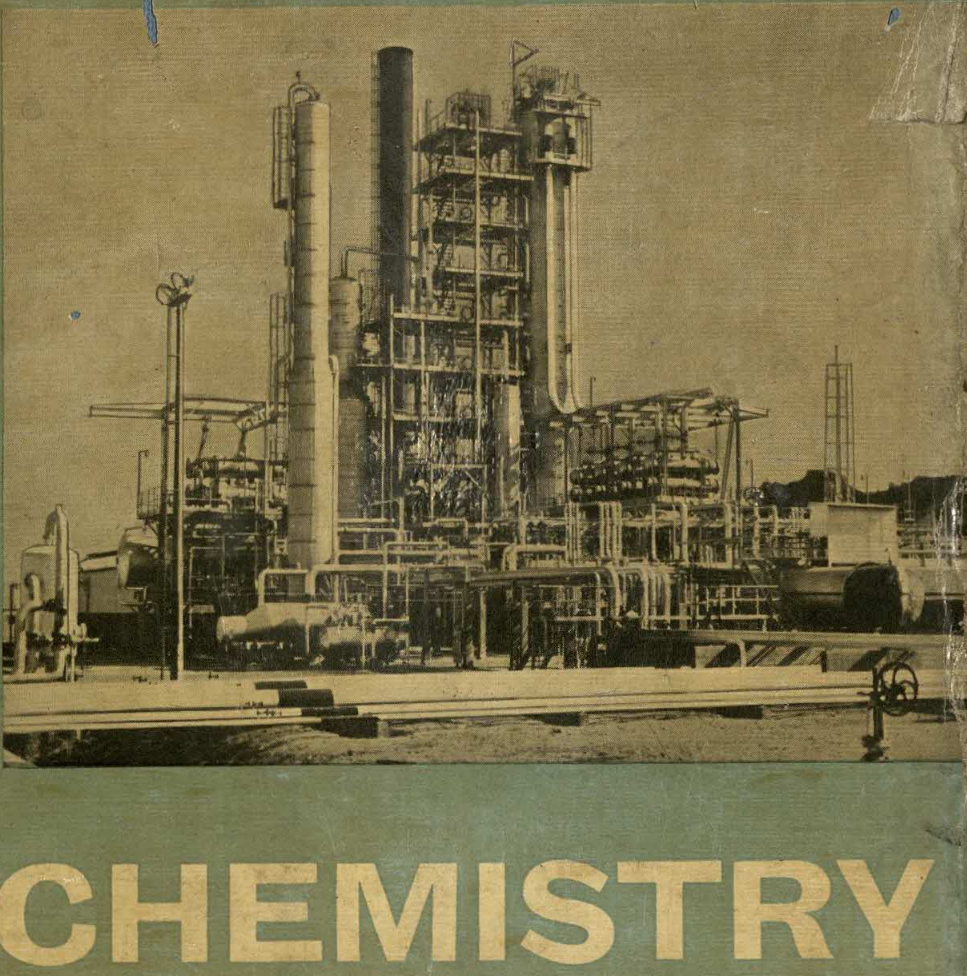
1030

ALEXANDER FINDLAY



CHEMISTRY
IN THE SERVICE OF MAN

EIGHTH EDITION

25/- net.

1030

This book was taken from the Library of Extension Services Department on the date last stamped. It is returnable within 7 days .

17.8.64

16.9.65

12.3.74

CHEMISTRY IN THE SERVICE OF MAN

By the same Author

INTRODUCTION TO PHYSICAL CHEMISTRY
PRACTICAL PHYSICAL CHEMISTRY

CHEMISTRY IN THE SERVICE OF MAN

BY

ALEXANDER FINDLAY
C.B.E., D.Sc., LL.D.
EMERITUS-PROFESSOR OF CHEMISTRY, UNIVERSITY OF ABERDEEN

EIGHTH EDITION

INSTITUTE OF EDUCATION FOR WOMEN
1030
Dept. of Extension
SERVICE.
CALCUTTA-27

540
Fin

LONGMANS, GREEN AND CO
LONDON · NEW YORK · TORONTO

LONGMANS, GREEN AND CO LTD
6 & 7 CLIFFORD STREET LONDON W 1
BOSTON HOUSE STRAND STREET CAPE TOWN
531 LITTLE COLLINS STREET MELBOURNE

LONGMANS, GREEN AND CO INC
55 FIFTH AVENUE NEW YORK 3

LONGMANS, GREEN AND CO
20 CRANFIELD ROAD TORONTO 16

ORIENT LONGMANS PRIVATE LTD
CALCUTTA BOMBAY MADRAS
DELHI VIJAYAWADA DACCA

BIBLIOGRAPHICAL NOTE

1st Edition - 1916
2nd Edition - 1917
3rd Edition - 1924
4th Edition - 1931
5th Edition - 1939
6th Edition - 1945
7th Edition - 1947
8th Edition - 1957

PRINTED IN GREAT BRITAIN
BY WESTERN PRINTING SERVICES LTD BRISTOL

TO
MY WIFE

"He that enlarges his curiosity after the works of Nature
demonstrably multiplies the inlets to happiness."

JOHNSON, *Rambler*, No. 5.

PREFACE TO THE EIGHTH EDITION

WHILE the main purpose of this book remains as stated in the Prefaces to the First and Seventh Editions, the opportunity has been taken of subjecting the text to a thorough revision. Various sections have been rewritten, shortened or amplified; and a considerable amount of rearrangement of the subject matter has been carried out so as to render the discussion more closely knit.

Some of the older and less important matter, such as the manufacture of matches and of paper, has been severely cut down in order to make room for a fuller discussion of more recent and interesting work on metals; drugs and antibiotics; insecticides; artificial fibres; vitamins and hormones; plant growth-regulating substances and nuclear energy.

It is, perhaps, noteworthy that for almost all the *practical* purposes of chemistry the atomic theory, as put forward by Dalton early in the nineteenth century, forms an adequate theoretical basis. I have, therefore, on the suggestion of one of my non-scientific readers, transferred what was formerly Chapter II to the end of the book. Here it forms a special chapter in which are discussed the new and wonderful ideas regarding the constitution of matter which have developed from a study of the discharge of electricity through rarefied gases and the discovery of the phenomenon of radioactivity. These ideas are not only altering men's thought and outlook on the world but are also opening up new avenues of investigation and yielding applications of the greatest social and industrial importance. In this chapter, also, is given a brief discussion of the principles underlying the utilization of nuclear energy in times of peace and of war.

At the present time, even as during and after World War I, there is much controversy regarding the place of science in the general education of the community. This book is therefore offered, in so far as chemistry is concerned, as a contribution towards repairing the failure, alluded to long ago by Mr. H. A. L. Fisher, when President of the Board of Education, 'to find a form of scientific instruction which might appeal to the imagination and interest of the general mass of the population . . . who are not destined for a specifically scientific career.' The form and content of the book, also, have been chosen so as to make appeal to the general reader of maturer years and to those engaged in the work of government and in the varied activities of administration who need or desire to understand something of the intellectual progress of recent years and to gain some knowledge of a branch of science on which much of our present-day civilization is based.

A.F.

66 Manor Way,
Beckenham, Kent.
February, 1956.

PREFACE TO THE SEVENTH EDITION

THIRTY-ONE years ago, when the preface to the first edition of this book was written, the author regarded it as his duty to emphasize how greatly we, as a nation, had thitherto failed to recognize the intimate and vital dependence of our social and national prosperity on a knowledge and appreciation of the facts and principles of science, and not least of chemistry, and on their application in industry. At the present time, we have every right to look back with a feeling of satisfaction—but certainly not of complacency, for much still remains to be done—on the great advances which have been made in this country during the past three decades in the encouragement and promotion of scientific research and in the application of science to the improvement of old and the development of new industries. Moreover, although this book is concerned with the advance of chemical science not only in this country but throughout the world, and with the service which chemistry has rendered to mankind, we, in this country, can feel proud of the part which British chemists have played in the general advance of the science no less than of its applications to the advantage of our industries and the material welfare of the people.

In times of war men are inclined to think of the work of chemists as being directed solely to destructive ends, but the discoveries of chemists are contributions to knowledge and, in themselves, are neither beneficent nor maleficent. It is in man's power and it is his responsibility, the responsibility of each individual citizen, to use these discoveries aright. The magnitude of the power which chemists have placed in the hands of men is a challenge to their moral greatness; and the greater the power the greater is man's opportunity for its right use and for high endeavour. The frightfulness of the atomic bomb, by which all men were appalled, should be a constant warning and should strengthen the admonition: 'Turn back, O Man, forswear thy foolish ways.'

Great as have been the suffering and destruction of life brought about by the misuse of the discoveries of chemists, very much greater have been the relief from suffering and the saving of life which their discoveries have made possible. Let the reader turn to *Chapter* 13 and let him try to compute the sum of misery, suffering and loss of life from which mankind has been saved by the anæsthetics, antiseptics, drugs and insecticides which we owe to the ability, trained intellect, scientific imagination and persistent endeavour of the chemist. It is no exaggeration to say that the health and well-being of the people are more fundamentally dependent on the chemist than on the physician.

In the following pages, also, it has been sought to give some account of the advances which have been made in elucidating the constitution of the atom and in opening up the prospect of the beneficent utilization of atomic energy, as well as of the recent achievements of chemists in other fields of social and industrial importance: light alloys, plastics, vitamins, hormones, etc.

While we should all be grateful for the many material benefits which chemical science has provided and for the service which it has rendered, and can in increasing measure still render, to industry, one must not fail to encourage or be niggardly in promoting the advance of science by investigations which are 'motivated solely by a desire to increase knowledge'; for the material benefits which derive from science are, as Cuvier said, 'applications of verities of a superior order, not sought with a practical intent, verities which their authors have pursued for their own sake, impelled solely by an ardour for knowledge.' Moreover, in our eagerness to achieve results of material value we must not lose sight of the idealism of science and of the intellectual satisfaction which its study can give. For the community as a whole it is of importance not so much that its individual members should acquire a knowledge of the practical applications of science as that they should become imbued with the spirit of science, the passion for truth and the forming of judgments on the basis of ascertainable facts, the spirit of co-operation, of tolerance, of charity and of unselfishness, which are the spirit of true scientific endeavour. The study of science ministers to the satisfaction of the intellectual need of the human mind to understand more fully the phenomena of nature, which become not less but more wonderful the more fully we learn their meaning. The interpretations of science, moreover, do not destroy but give significance to the beauty of nature.

A. F.

66 Manor Way,
Beckenham, Kent.
March, 1947.

PREFACE TO THE FIRST EDITION

When the writer was invited to deliver the Thomson Lectures before the United Free Church College, Aberdeen, at the end of the year 1915, he felt that, as a teacher of chemistry, he could attempt no higher task than that of giving to his hearers, who made no claim to chemical knowledge, some account of what the science of chemistry, both in its general principles and in its industrial applications, has accomplished for the material well-being and uplifting of mankind; and the lectures which were then delivered form the basis of the present work.

The reasons which prompted the choice of subject are, of course, not far to seek. The crisis through which this and other European countries are now passing has brought home to us how greatly we, as a nation, have hitherto failed to recognize the intimate and vital dependence of our social and national prosperity on a knowledge and appreciation of the facts and principles of science, and not least of chemistry, and on their application in industry. All the industries of the country on which not only the comfort but even the life of the people depend—the great manufacturing industries, and agriculture, the greatest industry of all—claim tribute of chemistry. And yet we, as a nation, have done much less than the responsibilities of our civilization demanded to promote and encourage the development of chemical knowledge; we have even, indeed, largely failed to avail ourselves of that tribute which science is so willing to pay. To the work of laying the foundation of pure science, on which the superstructure of successful industrial achievement must be raised, British chemists have, according to the measure of their numbers, contributed an honourable share; but the people as a whole, being ignorant of science, have mistrusted and looked askance at those who alone could enlarge the scope of their industries and increase the efficiency of their labours. And so we have witnessed in the past an appalling and needless waste of our national resources, and in too many cases industries have languished and succumbed, or, even when born under conditions of great promise, have remained dwarfed and stunted in growth. In 1862, the German chemist, Hofmann, at that time a Professor of Chemistry in London, could utter the prophecy: 'England will, beyond question, at no distant day, become herself the greatest colour-producing country in the world, nay, by the strangest of revolutions, she may, ere long, send her coal-derived blues to indigo-growing India, her tar-distilled crimsons to cochineal-producing Mexico, and her fossil substitutes for quercitron and safflower to China, Japan, and the other countries whence these articles are now derived.' But, alas! that prophecy has not yet been fulfilled, and the industry of synthetic dyes, an industry which above all others depends on the fostering and encouragement of chemical research and on the highest scientific efficiency, has found a home elsewhere amid more congenial surroundings.

But there are now welcome signs that the country is awakening to a sense of past deficiencies, and already the Government has taken a first short step in the direction of encouraging and assisting scientific and industrial research. But if the national effort is really to become effective and to exert a lasting influence, something more is necessary, something which is, perhaps, more difficult of achievement than Governmental aid. The mental outlook and the attitude of the people as a whole towards science must be changed, and the scientific habit and a spirit of trust in science must be cultivated; and we must also attract in much larger numbers into the ranks of scientific workers men of equal mental calibre to and capable of taking the same wide outlook as those who are at present attracted into the higher ranks of the legal profession or into the Civil Services. Science stands for efficiency *in all the activities of life*, and the neglect of science spells waste and industrial decay. It is for the country to choose the path which it will follow, but in making their choice let the people bear in mind the words spoken by the King when Prince of Wales: 'Does not experience warn us that the rule of thumb is dead, and the rule of science has taken its place; that to-day we cannot be satisfied with the crude methods which were sufficient for our forefathers, and that those great industries which do not keep abreast of the advance of science must surely and rapidly decline?'

But we must learn to appreciate science not merely on account of its utilitarian value as a means of increasing wealth and material prosperity. From the material point of view, doubtless, 'science is the knowledge most worth,' and in the case of most people, perhaps, interest in science centres round its industrial or economic utility. *Nisi utile est quod facias, stulta est gloria* ('All useless science is an empty boast') is a sentiment which will find a wide if not a universal acceptance, but we must beware of interpreting the usefulness of science in too narrow a spirit. The study of science possesses a cultural value which is quite independent of the utility of its applications; and as an instrument of culture, as a means of coming into closer relations with Nature and the Infinite, science claims a fuller and more widespread recognition.

At a time of awakening interest in science, the author hopes that the present attempt to give a readily intelligible account of some of the more important general principles and theories of chemical science and of their applications may afford to the general reader some idea of the world's indebtedness to the chemist, and may also stimulate the interest of, at least, the younger students of chemical science by presenting to them a picture of that land into a fuller possession of which they one day hope to enter.

My thanks are due to the publishers, Messrs. Longmans, Green & Co., for permission to use Figures 1, 2, 9, and 10, taken from works published by them; and I desire, also, to express my indebtedness to my wife for her assistance not only in preparing the manuscript for publication, but also in reading the proof-sheets.

A. F.

Y GLYN,
LLANFARIAN,
NR. ABERYSTWYTH.
March, 1916.

CONTENTS

CHAPTER 1

PAGE

INTRODUCTION

Definition and scope of chemistry. Constitution of matter. Alchemy. Iatrochemistry. Elements and compounds. Composition of the earth. Dalton's atomic theory. Molecules. Atomic weights. Symbols and formulæ. Mixtures and Compounds. Physical and chemical change. Valency. Periodic law. Modern scientific method 1

CHAPTER 2

THE GASES OF THE ATMOSPHERE

Composition of the atmosphere. Nitrogen. Oxygen. Carbon dioxide. Circulation of carbon in nature. RARE GASES. Argon. Identification of gases by spectroscopy. Helium. Neon. Krypton. Xenon. Liquefaction of air 21

CHAPTER 3

COMBUSTION AND THE PRODUCTION OF FIRE

Explanation of combustion in air. Phlogiston theory. Lavoisier's explanation. Ignition point. Safety lamp. Slow combustion. Combustion in the living organism. Spontaneous combustion. Combustion by means of combined oxygen. Thermit. Matches. Petrol-lighters 33

CHAPTER 4

FUEL AND ILLUMINANTS

SOLID FUELS—Calorific value. Wood. Peat. Coal. Smokeless fuel. Air pollution. SOLID ILLUMINANTS. Candles. LIQUID FUELS AND ILLUMINANTS. Petroleum. Saturated and unsaturated hydrocarbons. Refining petroleum. Cracking of oil. Octane number. Oil shale. Hydrogenation of coal. Synthetic production of oils. GASEOUS FUELS AND ILLUMINANTS. Natural Gas. Coal-gas. Luminosity of flame. Therms. Bunsen burner. Oxy-coal-gas flame. Complete gasification of coal. OTHER GASEOUS FUELS. Water-gas. Producer gas. Semi-water-gas. Hydrogen. Oxy-hydrogen flame. Production of rubies and sapphires. Atomic hydrogen flame. Hydrogen peroxide. Carbon monoxide. Acetylene. Incandescent gas-mantle . . 45

PAGE

CHAPTER 5

MATTER, ENERGY AND EXPLOSIVES

Energy of chemical reactions. Exothermal and endothermal reactions. Ozone. Allotropic forms of carbon. Diamond. Graphite. Crystalline structure. Charcoal. Carbon black. Explosives . 72

CHAPTER 6

METALS AND THEIR ALLOYS

Properties of metals. Seven metals of antiquity. Gold, silver and platinum. Vaporization in a high vacuum. Mirrors. Photography. Bromine. Iodine. Iron and steel. Portland cement. Copper and non-ferrous metals. Season cracking. Beryllium. Nickel. Cobalt. Chromium. Mercury. Tin. Zinc. Lead. Titanium. Tungsten. Germanium 86

CHAPTER 7

VELOCITY OF REACTIONS AND CATALYSIS

Chemical affinity. Influence of concentration. Law of mass action. Influence of temperature. Reversible reactions. Catalysis. Enzymes. Manufacture of sulphuric acid. Cement. Sulphur. Recovery of sulphur. Hydrogenation or hardening of oils. Margarine. Syntheses from water-gas. Hydrogen from methane. 105

CHAPTER 8

CHEMISTRY AND AGRICULTURE

Substances necessary for the growth of plants. Potassium salts. Phosphates. Nitrogenous fertilizers. Fixation of atmospheric nitrogen—1. Direct combination of nitrogen and oxygen; 2. Fixation of nitrogen by means of carbides; 3. Production of synthetic ammonia. Urea. Lime. Trace elements. Selective weed killers. Growth regulators. Catalytic oxidation of ammonia . . . 124

CHAPTER 9

GLASS, SODA, SOAP, LIME AND CLAY

Discovery of glass. States of matter. Crystalline and amorphous solids. Crystallization of liquids. Super-cooled liquids. Devitrification. SILICA AND GLASS. Water-glass. Glass. Annealing of glass. Toughened glass. Safety glass. Pyrex. Crystal glass. Strass or paste. Coloured glass. Silvering of glass. Glass wool. SODA. Manufacture of soda. Hydrochloric acid. Chlorine. Bleaching powder. SOAP. Saponification of fats. Manufacture of soap. Soft soap. Hard soap. Glycerine. Cleansing power of soap. Soapless detergents. Hard water. Softening of hard water. Permutit. Removal of salts from sea-water. LIME. Limestone caves. Stalactites and stalagmites. Quicklime. Slaked lime. Mortar. Limestone, chalk, coral, marble, Iceland spar, pearls. CLAY. Porcelain, stoneware, earthenware. Portland cement. Concrete 139

CHAPTER 10

ELECTRICITY AND CHEMISTRY

Voltaic cell. Sodium and potassium. Sodium cyanide. Electro-plating. Conduction of electricity by solutions. Electrolytes and non-electrolytes. Electrolysis. Ions. Movement of ions. Acid-alkali indicators. pH. Leclanché cell. Lead accumulator. Nickel-iron cell. Nickel-cadmium cell. Refining of copper. Manufacture of chlorine and of caustic soda. Hydrogen and oxygen. Fluorine. Aluminium. Anodizing. Alloys of aluminium. Magnesium. Carborundum. Alundum. Artificial graphite 164

CHAPTER 11

THE COLLOIDAL STATE

Analogy between solutions and gases. Diffusion. Colloids and crystalloids. The colloidal state. Tyndall phenomenon. The ultramicroscope. Ruby gold. Size of colloid particles. Adsorption. Chromatography. Emulsoids and suspensoids. Electrophoresis. Sedimentation in rivers. Process of dyeing. Mordants. Colloids in agriculture. Purification of water and sewage. Protective action of emulsoids. Peptization. Mass of the molecule. Brownian movement 182

CHAPTER 12

MOLECULAR ARCHITECTURE

Organic chemistry. Isomerism. Molecular constitution. Valency. Formulæ of Couper and of Kekulé. Optical activity. Stereo-chemistry. Theory of van't Hoff and Le Bel. Resolution of the racemic into the optically active forms. Stereo-chemistry and vitalism. Production of optically active compounds . . . 196

CHAPTER 13

DYES, PERFUMES, DRUGS AND INSECTICIDES

Chief constituents of coal-tar. The coal-tar dyes. Synthesis of alizarin. Synthesis of indigotin Tyrian purple. Synthetic perfumes. Anæsthetics, Antiseptics, Hypnotics, Drugs, Insecticides. Chloroform, novocaine, amethocaine; chloral, veronal, luminal; aspirin; salvarsan, tryparsamide, suramin, antrycide, plasmoquin (pamaquin), mepacrine (atebrin), paludrine, sulpha-drugs, dapsone (avlo-sulfon), solapsone (sulphetrone); penicillin, streptomycin, chloramphenicol, aureomycin, terramycin; pyrethrins, rotenone, DDT, gammexane, aldrin, dieldrin . . 215

CHAPTER 14

ARTIFICIAL FIBRES AND PLASTICS

Carbohydrates. Cellulose, xylose. Nitrocellulose, rayon. Staple fibre, Rayolanda. Cellophane. Mercerized cotton. Lanital. Ardil. Vicara. Nylon. Terylene. Orlon. Celluloid, cellon. Erinoid

PAGE

(galalith). Bakelite. Butvar. Beetle ware. Perspex. Polythene (alkathene). Polyvinyl chloride. Fluon (teflon). Polystyrene (distrene). Silicones. Rubber-like materials: vulcanite, isoprene, butadiene, buna, neoprene, chloroprene, alloprene. . . 236

CHAPTER 15

FERMENTATION AND THE ACTION OF ENZYMES AND MICRO-ORGANISMS

Explanation of fermentation. Enzymes. Manufacture of alcohol. Proof spirit. Methylated spirit. Saccharification of starch (amylo-process). Alcoholic beverages. Whisky, gin, brandy, rum. Wines. Beers. Fusel oils. Artificial fruit essences. Plasticizers. Vinegar. Acetic acid. Acetaldehyde. Acetone. Curdling of milk. Cheese. Casein. Distempers. Production of glycerine. Dextran 255

CHAPTER 16

VITAMINS AND HORMONES

Nutrition. Vitamins. Vitamin A. Carotene. Vitamin B_1. Thiamine (aneurine). Vitamin B_2-complex. Nicotinamide. Riboflavine. Vitamin C. Ascorbic acid. Vitamin D. Ergocalciferol (D_2), cholecalciferol (D_3). B_{12} (cyanocobalamin). Pyridoxin (B_6). Biotin (H). Tocopherol (E). Hormones. Adrenaline. Thyroxine. Thiouracil. Insulin. Sex hormones. Cortisone. ACTH. Trace elements. Plant growth-regulators. Selective weed killers. Parthenocarpy. Rooting of cuttings. Inhibition of potato sprouting. Premature dropping of fruit. 269

CHAPTER 17

FROM THE CROOKES TUBE TO THE NUCLEAR REACTOR

Cathode rays and electrons. Radioactivity. Radium. Alpha, beta and gamma rays. Disintegration theory. Atomic structure. Atomic number. Isotopes. Planetary electrons. Explanation of valency. Transmutation of the elements. Tracer elements. Nuclear energy. Nuclear fission. Atomic bomb. Nuclear fusion. Hydrogen bomb. Nuclear reactor 287

INDEX 311

PLATES

facing page

1. The Alchemist 48
Reproduced by courtesy of the Trustees, the National Gallery, London
2. Robert Boyle 48
National Portrait Gallery
3. John Dalton 48
Mansell Collection
4. Fire of Burning Oil 49
By courtesy of Foamite Ltd.
5. Oil Fire Extinguished by Foamite Firefoam 49
By courtesy of Foamite Ltd.
6. Antoine Laurent Lavoisier 64
Mansell Collection
7. A Peep at the Gaslights in Pall Mall 64
Picture Post Library
8. A Modern Petroleum Distillation Unit 65
By courtesy of the British Petroleum Company Ltd.
9. Cutting a Steel Shaft by an Oxy-acetylene Flame 65
By courtesy of the British Oxygen Co. Ltd.
10. A 20-Carat Cape Diamond Embedded in Blueground 112
11. Pans for Nitrating Cellulose 112
By courtesy of I.C.I. Ltd.
12. Blasting Rock in a Quarry 113
By permission of the Irish Press Ltd., Dublin
13. Blasting Rock in a Quarry 113
By courtesy of the Steetley Dynamite Co. Ltd.
14. Photograph Taken by Infra-red Light 128
By courtesy of Kodak Ltd.
15. Medal Showing Tin Plague 128
16. Effect of Potash Salts on the Growth of Mangolds 129
By permission of Rothamsted Experimental Station
17. Searles Lake, California 129
18. Effect of Nitrogenous Fertilizers (Ammonium Sulphate) on Plant Growth 129
By permission of Rothamsted Experimental Station

facing page

19. Selective Weed Control 176
By courtesy of Professor R. L. Wain

20. Castle Geyser, Yellowstone Park 176

21. Cracking of Ordinary Plate Glass 177
By courtesy of Pilkington Bros., Ltd.

22. Cracking of 'Armourplate' Glass 177
By courtesy of Pilkington Bros., Ltd.

23. Fibreglass Insulation of Electric Cable 177
By courtesy of Owens-Corning Fiberglas Corporation

24. Manufacture of Soap 192
By courtesy of Lever Brothers, Ltd.

25. Ribbons of Soap being Scraped Off Chilling Roller 192
By courtesy of Lever Brothers, Ltd.

26. Extrusion of Soap in Form of Bars 192
By courtesy of Lever Brothers, Ltd.

27. Limestone Terraces, Yellowstone Park 193
By courtesy of the Union Pacific Railroad Company

28. Iceland Spar, Showing Double Refraction 193

29. Production of Hydrogen and Oxygen by Electrolysis 240
By courtesy of the International Electrolytic Plant Co. Ltd.

30. Figure of Eros on Shaftesbury Fountain, London 240
By courtesy of the Aluminium Development Association

31. Louis Pasteur 241
Mansell Collection

32. Spraying Insecticides from a Helicopter 241
By courtesy of Fisons Pest Control Ltd.

33. Tablets of Paludrine in Alkathene Envelopes 256
By courtesy of I.C.I. Ltd.

34. Polythene Squeeze-bottle 256
By courtesy of E. Shipton and Co. Ltd.

35. 'Pine' Disease in Lambs 257

36. Photograph of Binoculars by Gamma Rays 257
By courtesy of the Atomic Energy Research Establishment

Chapter 1

INTRODUCTION

CHEMISTRY is a branch of science which deals with matter, or with the material universe which is revealed to us by our senses. It studies the different kinds of substances found in the world, whether in the living animal and plant organisms, or in the non-living mineral matter of the universe. Chemistry investigates the composition and specific properties of these substances, the methods of their preparation, the changes which they undergo, and their behaviour, not only when acted upon by what are called physical forces (heat, light, electricity, etc.), but also in reaction with other substances; and it studies also how, from the materials already known, new materials may be obtained. Through a knowledge of chemistry one may learn how to prepare, artificially, substances which occur ready formed in nature, or how to prepare substitutes for these naturally-occurring substances. Chemistry, further, occupies itself with the question of how materials already manufactured can be manufactured more economically, or be replaced by more suitable materials; and it helps us to understand how the natural and, it may be, irreplaceable resources of the world can be economized. On the science of chemistry, more than on any other branch of organized knowledge, depend the material well-being and comfort of man.

But the end and aim of chemistry is not merely material. Chemistry offers its contribution also to the deeper interests of the human mind. Occupied as he is with the study of material substances and of the marvellous transformations which he is able to bring about in them, the thinking chemist is forced to look beneath the surface of things and to seek an answer to the fundamental questions relating to the ultimate constitution and structure of matter and to the forces which govern the changes and transformations which he observes in his laboratory, or which are wrought out in the larger laboratory of Nature. The study, not merely of the *products* but also of the principles and laws underlying the *processes* of chemical change, forms the work of the modern chemist.[1] In its wider sweep, chemistry ignores the conventional and artificial frontiers which mark it off from the other branches of science, more especially physics; and during the present century there have been no more fruitful regions of experimental and speculative activity than those common territories where, for example, the sciences of chemistry and physics and chemistry and biology overlap.

Chemistry, in its idealistic quest of truth about nature, possesses a cultural value apart from its applications. Its study is not only a means of cultivating the mind and of training and strengthening the scientific habit of thought, but it also brings us into closer relations with and gives a fuller understanding of the physical universe in which we live. From this we can derive both intellectual satisfaction and an æsthetic pleasure. In attempting, therefore, a brief and necessarily incomplete survey of chemistry in the service of man, I shall endeavour not merely to recount some of the manifold ways in which chemistry has revolutionized life and has contributed, on the material side, to a civilized existence; but I shall try, also, to indicate, if I cannot do more, some of the principles which underlie chemical change, and to recount some of the achievements of chemists and physicists who, during the present century, with amazing insight and experimental skill, have been making known to us the invisible texture of what Carlyle called 'the Time-vesture of the Eternal,' the material universe.

THE CONSTITUTION OF MATTER

The problem of the constitution of matter is one which has occupied men's minds from the earliest beginnings of philosophic enquiry; and in the philosophic epoch of the development of our knowledge of the material universe, one cannot but recognize the pre-eminence of ancient Greece. Men of other races and of earlier civilizations had doubtless speculated on the problem of the ultimate constitution of matter, but it was in Greece that the streams of thought flowing from Chaldea, from India and from Egypt, met and mingled, settled and became clarified. It is in ancient Greek philosophy that we find formulated most clearly many of the problems which face the modern man of science, and it was by the Greek philosophers that the first important attempts were made at their solution. These philosophers, it is true, could not make any very marked advance in their knowledge of the physical universe, and their theories remained to a great extent unfruitful, simply because their knowledge of facts was too slight and there was no possibility of testing the validity of their theories by experiment. Nevertheless, channels of thought were cleared by them and lines of advance were opened for others who through difference of temperament and outlook, as well as by growth of knowledge, were perhaps more fitted to travel along them.

---

[1] In Great Britain some confusion is caused by the fact that the word chemist is used with two different meanings. On the one hand it is used for one who prepares and retails drugs—a druggist or pharmacist; and on the other hand, it denotes one who pursues the study and advances a knowledge of the science of chemistry. It is with the latter meaning that the word is used throughout this book.

Many and varied were the views which were held, and although the study of these will always prove interesting, it must be borne in mind that the considerations which governed the speculations of many of the ancient philosophers were quite different from those by which the modern scientist feels himself bound. To many of the Greek philosophers, the fact that our eyes make things manifest to us was no proof that those things exist. By them, intuition, a very valuable gift indeed, and reason were made the all-sufficient grounds of knowledge; and they sought to explain the universe by the exercise of a vigorous imagination and a rigorous logic. One cannot therefore wonder that they sometimes lost touch with reality. As has been said: 'The intellectual vigour of the philosophers of antiquity, indeed, was capable of the grandest and most comprehensive views of Nature, and often conducted them to the most sublime truths, but in attempting perpetually to soar above the vulgar paths of observation and experience, they speedily became confounded in the mists of error and conceit.'

In the philosophy of ARISTOTLE, based on that of EMPEDOCLES, we find the conception of one primordial matter, *æther*, which acted as the carrier of certain essential qualities which were taken to be hotness, coldness, wetness, dryness; and the combination of these qualities in pairs was supposed to give rise to the four elements or primary forms of matter, *fire* (hot and dry), *air* (hot and wet), *earth* (cold and dry), *water* (cold and wet). The elements were regarded not as material things but rather as combinations of the essential qualities; and by the union of these in different proportions the different substances were considered to have been formed. This conception of the constitution of matter dominated science until the time of ROBERT BOYLE in the seventeenth century; and the idea of the existence of four 'elements' (fire, air, earth, water) lingers on, in popular thought, even to the present day.

During a period of many centuries before the beginning of the Christian era, Egyptian craftsmen had acquired great skill and expertness in the extraction and working of metals, and had achieved much success in the surface-colouring of metals and in the production of alloys which counterfeited the appearance of gold and silver. In Alexandria, in the early years of the Christian era, Egyptian technical knowledge became united with Greek philosophic speculation and with the astrological and mystical views of the Chaldeans; and from Alexandria this body of knowledge, speculation and mysticism passed to Syria and Persia, and later, in the seventh century, to Arabia. To the Greek word, *chemeia*,[1] applied to the art of making or counterfeiting gold and silver, the Arabs prefixed the article *al*, and so gave us the term *alchemy*.

Alchemy was, from the very beginning, not only an art but a philosophy, and the philosophic basis of alchemy is to be found in the Aristotelian doctrine of the essential unity of matter, and the view that matter is merely the carrier or embodiment of certain qualities which could be removed from one form of matter and transferred to another form of matter. The belief in the transmutability of matter, in the transmutability, for example, of lead into gold, followed naturally from the Aristotelian theory.

The alchemists also reasoned much by analogy and were thereby often led woefully astray. Thus it was thought that just as in the case of animals birth and growth occur, so also in the mineral world metals were thought of as being generated and growing in the earth; and just as a chicken grows from an egg, so

---

[1] This word is probably derived from *chemi* (meaning black), the ancient name given to Egypt on account of the dark colour of its soil.

The same we say of lead, and other metalls,
Which would be gold, if they had time.
. . . for 'twere absurd
To think that nature, in the earth bred gold
Perfect i' the instant. Something went before.[1]

How absurd these views would seem to be; and yet, although the alchemists were misled by a false analogy, recent work on artificial transmutation (*Chap.* 17) shows that the idea of 'growth' in minerals is not so fantastic as at one time it appeared to be.

The production of gold, the perfect and complete metal, was regarded as being the end and aim of Nature's striving;[2] and it was the aim of the alchemists to hasten the process of growth of imperfect or base metals into gold by means of a medicine or transmuting agent called the philosopher's stone, the elixir, the magisterium, etc. To obtain this, all the kingdoms of nature—animal, vegetable and mineral—were ransacked; and materials of all kinds were calcined, boiled, fused and distilled.

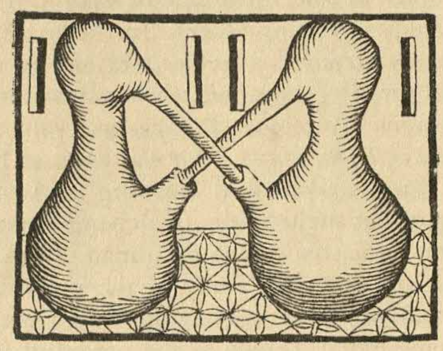


FIG. 1.—A SIXTEENTH-CENTURY TWIN 'PELICAN,' OR CIRCULATORY VESSEL, FOR THE PROLONGED HEATING OF LIQUIDS

Alchemy, then, was a philosophy of nature, and to many of the scholars of the Middle Ages, such as ALBERTUS MAGNUS and ROGER BACON, it made chiefly an intellectual appeal. There were many others, however, for whom avarice and cupidity were the loadstars, and in the fifteenth and sixteenth centuries, especially, alchemy passed into the hands of visionaries and swindlers. Europe swarmed with rogues and tricksters, and it is they who have caused alchemy to be associated in men's minds only with deceit, quackery and charlatanism (Plate 1).

---

[1] Ben Jonson: *The Alchemist.*

[2] The occurrence of gold and silver in association with base metals, such as copper and lead, was held to support the view that base metals grow into the metals silver and gold.

Although the alchemists failed in their endeavour to transmute the base metals into gold, yet by their unceasing labour they laid the foundations of present-day chemistry. To the alchemists we owe the preparation of substances of supreme importance in chemical science, such as sulphuric acid or oil of vitriol; hydrochloric acid or spirit of salt; nitric acid or *aqua fortis*; *aqua regia*, the solvent of gold, and many others. In the sixteenth century, moreover, alchemy acquired a nobler aim and ideal under the influence of that erratic genius and rebel against convention and tradition—Philippus Aureolus Bombastus von Hohenheim, generally known as PARACELSUS, who was born at Einsiedeln in Switzerland in 1493, and died at Salzburg in Austria in 1541. Paracelsus taught that the true aim of alchemy should be, as the handmaid of medicine, the curing of human illness and disease, and that the preparation and study of the properties of drugs should be the main object of the chemist. A new era in chemistry was thereby inaugurated, known as the period of *iatrochemistry* or medical chemistry.

The teachings of Paracelsus not only turned men's minds from the obsession of gold-making and 'the deceitful and mischievous art of alchemy,' but led also to the preparation and study of many new materials. Iatrochemistry acted as the bridge between the alchemy of the fifteenth century and the beginnings of an exact science of chemistry in the seventeenth century.

The philosophy of Aristotle held sway in the minds of men and as a dogma of the Church throughout the Middle Ages, but from time to time protests were raised against the doctrine of the four elements; and the overthrow of this philosophy was completed in the seventeenth century by the Hon. ROBERT BOYLE,[1] of whom it has been said that 'he was the father of chemistry and son of the Earl of Cork' (Plate 2).

---

[1] Robert Boyle, youngest son of the first Earl of Cork, was born at Lismore, Ireland, in 1627, and died in 1691. He was the author of *The Sceptical Chymist*, the publication of which, in 1661, marks the beginning of chemistry as a science.

Pure substances, Boyle pointed out, can be divided into two classes. In the one class are those which have, so far, resisted all attempts to decompose them, or to break them down into substances simpler than themselves. These substances, according to Boyle, are the true *elements*, and this definition of an

LIST OF THE ELEMENTS

Atomic number	*Symbol*	*Atomic weight*	*Atomic number*	*Symbol*	*Atomic weight*
1. Hydrogen	H	1·008	47. Silver	Ag	107·88
2. Helium	He	4·003	48. Cadmium	Cd	112·41
3. Lithium	Li	6·94	49. Indium	In	114·76
4. Beryllium	Be	9·013	50. Tin	Sn	118·70
5. Boron	B	10·82	51. Antimony	Sb	121·76
6. Carbon	C	12·01	52. Tellurium	Te	127·61
7. Nitrogen	N	14·008	53. Iodine	I	126·92
8. Oxygen	O	16·00	54. Xenon	Xe	131·3
9. Fluorine	F	19·00	55. Caesium	Cs	132·91
10. Neon	Ne	20·183	56. Barium	Ba	137·36
11. Sodium	Na	22·997	57. Lanthanum	La	138·92
12. Magnesium	Mg	24·32	58. Cerium	Ce	140·13
13. Aluminium	Al	26·97	59. Praseodymium	Pr	140·92
14. Silicon	Si	28·06	60. Neodymium	Nd	144·27
15. Phosphorus	P	30·98	61. Promethium	Pm	147
16. Sulphur	S	32·066	62. Samarium	Sa	150·43
17. Chlorine	Cl	35·457	63. Europium	Eu	152·0
18. Argon	A	39·944	64. Gadolinium	Gd	156·9
19. Potassium	K	39·096	65. Terbium	Tb	159·2
20. Calcium	Ca	40·08	66. Dysprosium	Dy	162·46
21. Scandium	Sc	45·10	67. Holmium	Ho	164·94
22. Titanium	Ti	47·90	68. Erbium	Er	167·2
23. Vanadium	V	50·95	69. Thulium	Tm	169·4
24. Chromium	Cr	52·01	70. Ytterbium	Yb	173·04
25. Manganese	Mn	54·93	71. Lutetium	Lu	174·99
26. Iron	Fe	55·85	72. Hafnium	Hf	178·6
27. Cobalt	Co	58·94	73. Tantalum	Ta	180·88
28. Nickel	Ni	58·69	74. Tungsten	W	183·92
29. Copper	Cu	63·54	75. Rhenium	Re	186·31
30. Zinc	Zn	65·38	76. Osmium	Os	190·2
31. Gallium	Ga	69·72	77. Iridium	Ir	193·1
32. Germanium	Ge	72·60	78. Platinum	Pt	195·23
33. Arsenic	As	74·91	79. Gold	Au	197·2
34. Selenium	Se	78·96	80. Mercury	Hg	200·61
35. Bromine	Br	79·916	81. Thallium	Tl	204·39
36. Krypton	Kr	83·7	82. Lead	Pb	207·21
37. Rubidium	Rb	85·48	83. Bismuth	Bi	209·0
38. Strontium	Sr	87·63	84. Polonium	Po	210
39. Yttrium	Yt	88·92	85. Astatine	At	210
40. Zirconium	Zr	91·22	86. Radon	Rn	222
41. Niobium	Nb	92·91	87. Francium	Fr	223
42. Molybdenum	Mo	95·95	88. Radium	Ra	226·05
43. Technetium	Tc	99	89. Actinium	Ac	227
44. Ruthenium	Ru	101·7	90. Thorium	Th	232·12
45. Rhodium	Rh	102·91	91. Protactinium	Pa	231
46. Palladium	Pd	106·7	92. Uranium	U	238·07

element is still retained. The definition, it should be noted, does not postulate the impossibility of decomposition, but insists merely on the fact that the possibility, if it exists, has not so far been realized.[1]

In the second class of pure substances are placed those which, by one means or another, can be resolved into simpler substances. These more complex substances are called *compounds*. Thus, for example, if the red substance, oxide of mercury, is heated in a glass tube, a gas is given off which has the property that it will cause a glowing splint of wood to re-ignite; and, at the same time, metallic mercury is deposited in shining droplets on the cooler portions of the tube. The red substance has thus been decomposed into metallic mercury and a gaseous substance, to which the name of oxygen has been given. This red substance, therefore, is a compound of mercury and oxygen.

Slowly the importance of distinguishing between elements and compounds was recognized and the work of *analysing* and of classifying the different kinds of matter and of determining the proportions in which elements combine to form compounds was pursued with great activity by chemists. In spite of the most laborious and prolonged efforts, chemists have not succeeded in reducing the number of the elements occurring in nature to less than about ninety. Of these ninety elements all the substances in the known universe are built up. For convenience of future reference a list of these elements, twenty-two of which were discovered by British chemists, is given on p. 7.

The elements technetium and promethium have not been found to occur in nature, but isotopes (*Chap.* 17) of these elements have been produced artificially.

To the list of elements on p. 7 may be added no fewer than nine elements which are known only as products of atomic transmutation (*Chap.* 17). They are:

93. Neptunium
94. Plutonium
95. Americium
96. Curium
97. Berkelium
98. Californium
99. Einsteinium
100. Fermium
101. Mendelevium

It may be that still other elements will be similarly produced.

---

[1] Although this definition may still serve for most purposes, the phenomena of radioactivity and the existence of isotopes, to which reference is made in the concluding chapter, show the need of a new definition.

Only about twenty of the elements occur free or uncombined in nature; and the amounts in which the different elements exist vary very greatly. Of all the elements found in the earth, the seas and the air, oxygen and silicon are by far the most abundant, as the following analysis shows:

CHEMICAL COMPOSITION OF TERRESTRIAL MATTER

(Earth, Air and Sea)

	per cent.		per cent.
Oxygen	50·02	Potassium	2·28
Silicon	25·80	Magnesium	2·08
Aluminium	7·30	Hydrogen	0·95
Iron	4·18	Titanium	0·43
Calcium	3·22	Chlorine	0·20
Sodium	2·36	Carbon	0·18
			99·00

From the numbers in this table one learns that the two elements, oxygen and silicon, in the free or in the combined state, constitute together three-quarters of the whole of terrestrial matter, by weight, so far as this is accessible to direct investigation.

If one considers the composition merely of the earth's crust accessible to investigation, the average values do not differ greatly from those given above. There is, however, evidence to show that the composition of the interior of the earth is very different from that of the crust; and, from investigations of different kinds, the conclusion has been drawn that beneath the crust of the earth there occur zones diminishingly rich in silicates and increasingly rich in iron, and that there is lastly a core consisting essentially of iron and nickel.

THE ATOMIC THEORY

Underlying the philosophy of Aristotle was the idea that matter is continuous and capable of infinite subdivision; but with the overthrow of the doctrine of the four elements of Aristotle there was revived another ancient hypothesis which had been put forward in the fifth and fourth centuries B.C., by LEUCIPPUS, DEMOCRITUS and EPICURUS. According to the doctrine of these philosophers, a doctrine which comes nearer to modern scientific views than any other system of philosophy of the ancient world, and which has been preserved and expounded for us by the Roman poet LUCRETIUS, matter is made up of indivisible particles, the 'atoms' or the 'first-beginnings of things.' These 'atoms' are immutable and eternal and are in constant motion, travelling through void. By the coming together of these atoms the substances constituting the material world were regarded as being formed; and the diversity of substances was held to be due to differences in the size and shape of the atoms composing the substances. 'Now mark and next in order apprehend of what kind and how widely differing in their forms are the beginnings of things, how varied by manifold diversities of shape. . . . The things which are able to affect the senses pleasantly consist of smooth and round elements; while all those, on the other hand, which are found to be bitter and harsh, are held in connection by particles that are more hooked, and for this reason are wont to tear open passages into our senses.'[1]

These views must seem crude to the modern mind, and even NEWTON, at the end of the seventeenth century, could not greatly refine them. Thus he expressed the view: 'It seems probable to me that God, in the beginning, formed matter in solid massy, hard, impenetrable, movable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as most conduced to the end for which He formed them; and that those primitive particles, being solids, are incomparably harder than any porous bodies compounded of them; even so very hard as never to wear or break in pieces, no ordinary power being able to divide what God Himself made one in the first creation.'

The great authority of Newton gave powerful support to the atomic conception of matter, but it was not till the beginning of the nineteenth century that this fundamental hypothesis was developed into a theory by which the observed phenomena and the laws of chemical combination, determined experimentally, could be *quantitatively* explained or co-ordinated. It was only after this had been done, however, that the general hypothesis of the atomic constitution of matter could become of any real value in science; and nothing has influenced the progress of chemistry so much as the achievement of this by the Manchester schoolmaster, JOHN DALTON[1] (Plate 3).

---

[1] Lucretius: *De rerum natura*, translation by Munro.

To the older philosophers, the atoms or indivisible particles into which matter could be divided all consisted of the same primordial material, although differing in size and shape. The atoms of Dalton, however, differed in their nature. In the case of any particular element, the definition of which has already been given, the atoms were assumed to be all exactly alike in their properties, including, of course, their mass; but they differed from the atoms of every other element.

Further, according to Dalton, a compound is formed by the combination of atoms of different kinds; and since the nature of the compound will necessarily depend on the number and kind of the atoms present, *the composition of the compound must be definite*. This is the first fundamental law of chemistry, the LAW OF CONSTANT PROPORTIONS.

And still further. Since the fundamental assumption of the atomic theory is that atoms are indivisible and cannot be broken up into anything smaller, it follows that if one particular element A combines with another element B to form compounds containing different proportions of A and B, these different proportions stand to one another in the ratio of integral, or whole, numbers. That is to say, we can have the compounds $A + B$, $A + 2B$, $2A + B$, $2A + 3B$, etc., where A and B represent atoms of the elements A and B. Here, then, we have the explanation of the second fundamental law of chemistry, the LAW OF MULTIPLE PROPORTIONS.

At first Dalton made no distinction between the smallest particle of an element and the smallest particle of a compound. Both were called atoms. But it is clear that this must cause difficulty, because although the atom of an element may be regarded as indivisible, the atom of a compound must still be capable of being split up into smaller particles, namely, the atoms of the component elements. A new name was therefore introduced in 1811 by the Italian physicist, AVOGADRO, who called the smallest particle of a compound a *molecule*. The molecule of a compound, therefore, consists of a number of elementary atoms. We have, then, the definition that an atom is the smallest particle of an element which can enter into the composition of a molecule, or which can take part in chemical exchange. It is, so to speak, the smallest coin in chemical currency. A molecule, on the other hand, is defined as the smallest particle of a substance, elementary or compound, *which can exist in the free state.*

---

[1] John Dalton, the son of a hand-loom weaver in Cumberland, was born in 1766. After teaching for some years in a Manchester school he became a private tutor. The atomic theory, on which his fame mainly rests, was formulated in 1803 and published in 1807. He died in 1844.

In some cases the atom and molecule of an element mean the same thing. Thus, the atoms of argon and helium, for example, can exist in the free state, by reason of the fact that they possess no power of combination. In very many cases, however, the free atoms of an element combine together to form aggregates of like atoms, so that the molecule of an element, or the smallest particle of the element capable of free existence, may consist of two or three or even of four atoms combined together.

The atomic theory of Dalton, modified by the conception of molecules, served to co-ordinate or explain the fundamental laws of chemistry, the laws of definite and of multiple proportions; and it enabled one also to understand the changes which accompany the formation and decomposition of compounds and the mutual reactions between compounds. On the basis of this theory the superstructure of modern chemistry was largely built.

Towards the end of last century, as we shall learn more fully in the concluding chapter, facts began to be encountered which were not in harmony with Dalton's simple concept of an atom as an eternal, indivisible particle. Nevertheless, although the atom of an element is now believed to be a more or less complex system of particles, the different systems of particles constituting the atoms of the elements are, for the most part, quite stable. For almost all the *practical* purposes of chemistry, therefore, one can still make use of Dalton's atomic theory and can regard the atoms of the elements as indivisible particles.

Atomic Weights.—According to the atomic theory of Dalton, the atoms of a particular element have a definite mass or weight, but although, on the basis of various experimental investigations, the absolute masses of atoms have been *calculated* (p. 289), one cannot determine these masses by direct weighing. It is, however, comparatively easy to determine the *relative* weights of the atoms, and such determinations constitute one of the greatest achievements of science which followed in the train of Dalton's atomic theory. These relative weights are what are called the *atomic weights* of the elements; and their values, referred to the value 16·00 as the atomic weight of oxygen, are given in the table on p. 7.

Symbols and Formulæ.—In the table on p.7, it will be seen that opposite each element is a letter or group of two letters, by means of which one can represent shortly the particular element. Each of these *symbols*,[1] as they are called, represents an atom of the particular element; and since a compound is regarded as being formed by the combination of atoms, one can conveniently represent the *molecule* of a compound by writing the symbols of the constituent atoms side by side. Thus, NaCl represents a compound of sodium and chlorine, the molecule of which consists of one atom of sodium and one atom of chlorine; CO, similarly, represents a compound of carbon and oxygen, and so on. Frequently, however, the molecule of a compound is formed by the combination of elements in more than one atomic proportion, and so one writes, for example, H_2O, which is the *formula*[2] for water; a formula which indicates that the molecule of water consists of two atoms of hydrogen united to one atom of oxygen. The formula NH_3, similarly, which is the formula for ammonia, indicates that the molecule of this compound consists of three atoms of hydrogen united to one atom of nitrogen.

In the same way one can represent the number of atoms in the molecule of an element. Thus, H_2, O_2, N_2, represent a molecule of hydrogen, oxygen and nitrogen respectively, and show that a molecule of each of these elements consists of two atoms. The molecule of phosphorus, however, consists of four atoms and is represented by P_4.

---

[1] These symbols were introduced early last century by the Swedish chemist, Berzelius, who used the initial letter of the Latin name to represent the element. Where the name of more than one element began with the same letter, a second letter was added as a distinguishing mark. By using the Latin names of the elements, the symbols were rendered international; and one can thus understand why, in certain cases, the symbols are not obvious abbreviations of the English name of the element. Thus, we have Sb=antimony (stibium); Cu=copper (cuprum); Au=gold (aurum); Fe=iron (ferrum); Pb=lead (plumbum); Hg=mercury (hydrargyrum); K=potassium (kalium); Ag=silver (argentum); Na=sodium (natrium); Sn=tin (stannum). The names of more modern elements are decided by international agreement.

[2] One speaks of the *symbol* of an element and the *formula* of a compound or of a molecule.

The use of these symbols and formulæ is a great convenience and renders much assistance to the chemist in understanding and in representing chemical changes; and they will be employed to some extent in the following pages. They will, however, be used to assist the understanding, not to burden the memory.

By the introduction of the idea of atomic weights, a new and extended meaning is given to chemical symbols and formulæ. The symbol, Na, for example, not merely represents the element sodium, but stands for one atomic proportion or 22·997 parts by weight of sodium. The formula, NaCl, similarly is not merely a convenient shorthand symbol for a compound, the molecule of which consists of one atom of sodium and one atom of chlorine—the compound sodium chloride or common salt—but it stands for one molecular proportion by weight, or 22·997 + 35·457 = 58·454 parts by weight of sodium chloride, the numbers 22·997 and 35·457 being the atomic weights of sodium and chlorine respectively. It will be clear, also, that the *molecular weight* of a compound, which is equal to the sum of the atomic weights of the elements forming it, is the weight of a molecule relatively to the weight of an atom of the standard element, oxygen, taken as 16·00.

It should always be borne in mind that when elements unite chemically or combine to form a compound, they lose their individual identities and their characteristics as elements. A distinction is thus given between a chemical compound and a mixture. For example: when iron powder and flowers of sulphur are mixed, a greenish-grey powder is obtained. The iron and the sulphur each retains its elementary properties, and the constituents can be separated by means of a magnet (which removes the iron), or by means of the liquid, carbon disulphide, which dissolves the sulphur. If, however, the mixture of iron and sulphur is heated, combination takes place, and a black compound is formed from which iron and sulphur can no longer be separated by means of a magnet or of carbon disulphide. Similarly, when the soft, silver-like metal, sodium, which reacts vigorously with water with liberation of hydrogen, combines with the yellowish-green-coloured, choking gas chlorine, the white crystalline *compound*, sodium chloride or common salt, which possesses the properties neither of sodium nor of chlorine, is formed.

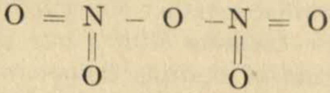
With the introduction of the atomic and molecular theories, it was realized that chemical change involves or is associated with change in the atomic groupings, or changes in the composition of the molecules of which the compounds are built up. Chemical change can, therefore, be distinguished from physical change, which involves no change in composition.

Valency.—Although atoms can combine with one another to form compounds, it has been established that elementary atoms do not possess an unlimited power of combination. The atoms of two different elements may combine in more than one proportion, but not in every proportion. Hydrogen and chlorine, for example, can combine together only atom for atom: an atom of hydrogen cannot combine with more than one atom of chlorine, and an atom of chlorine cannot combine with more than one atom of hydrogen. On the other hand, an atom of the metal calcium can combine with two atoms of chlorine to form the compound calcium chloride ($CaCl_2$); an atom of aluminium can combine with three atoms of chlorine to give $AlCl_3$; and an atom of carbon can combine with four atoms of chlorine to form carbon tetrachloride, CCl_4. The atoms of different elements, therefore, have a certain combining capacity, or have a certain *valence*[1] or *valency*, as it is called; and since one atomic proportion of hydrogen is never known to combine with more than one atomic proportion of any other element, the combining capacity or valence of hydrogen is taken as the standard and put equal to unity. Chlorine, an atom of which can combine with only one atom of hydrogen, is also said to have unit valence or to be univalent. Oxygen, an atom of which can combine with two atoms of hydrogen (as in water, H_2O), is said to be bivalent; nitrogen, an atom of which can combine with three atoms of hydrogen (as in ammonia, NH_3), is said to be trivalent; carbon, an atom of which can combine with four atoms of hydrogen, is said to be quadrivalent; and so on.

The concept of valency implies that the constituent atoms of a compound are not clumped together haphazardly, like a handful of marbles, to form the molecule of the compound. They must be attached or linked together in some orderly manner, in accordance with their valency, to form a definite pattern; and this molecular pattern can be represented by means of what are called *graphic formulæ.* In these formulæ the mutual attachments or linkings of the atoms are indicated by dots or lines (called 'bonds'), each dot or line representing the union of two valencies (as if they were clasping hands), one from each of the linked atoms. Thus one may represent the molecule of water by the graphic formula, H–O–H, and that of carbon dioxide by O:C:O. In the latter case, the atoms are linked by *double bonds*, the two valency bonds of each oxygen atom uniting with two of the four valency bonds of carbon. In like manner the more complex molecule, for example, of nitrogen pentoxide, N_2O_5, can be represented by the graphic formula:

---

[1] From the Latin *valere*, to be worth.



$$\begin{array}{ccccccccc} O & = & N & - & O & - & N & = & O \\ & & \| & & & & \| & & \\ & & O & & & & O & & \end{array}$$

In this compound nitrogen is quinquevalent, and each nitrogen atom has five bonds, or clasping hands; each oxygen atom has two. (See also *Chap.* 12.)

The doctrine of valency, first clearly stated by Sir Edward Frankland in 1852, was put forward as an empirical doctrine, and it is only during the present century that a theoretical basis was found for it in the conception of the electronic constitution of matter which will be discussed in *Chap.* 17.

The Periodic Law.—For the application of the atomic theory, according to which the atomic weights are fundamental units of chemical science, the determination of these relative weights of the atoms was a matter of the highest importance. By 1858, general agreement on these values had been reached, and their study brought to light a number of regularities and relationships which pointed to the existence of some genetic connection between the elements; and of these regularities the most important was that discovered by the Russian chemist, Mendeléeff, and by the German chemist, Lothar Meyer, in 1869 and 1870, the so-called *periodic law.* It was observed by these chemists that when the elements are arranged in the order of their atomic weights, there is a periodic recurrence of properties. Thus, leaving hydrogen and helium out of account for the present, and starting with lithium, we have the series,

lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, neon,

and then the series,

sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, argon,

in which the properties of the elements are similar to those of the corresponding members of the former series; that is, sodium is similar to lithium, magnesium to beryllium, and so on till we come to argon which has properties similar to those of neon. After argon there comes the element potassium,[1] and a new series is begun. Now, however, as the diagram (Fig. 2) shows, new types of elements occur and the period becomes longer, so that, from potassium, which corresponds to lithium and sodium on the one hand, to krypton, which corresponds to neon and argon on the other hand, there is a period not of eight but of eighteen elements. This is followed by another period of

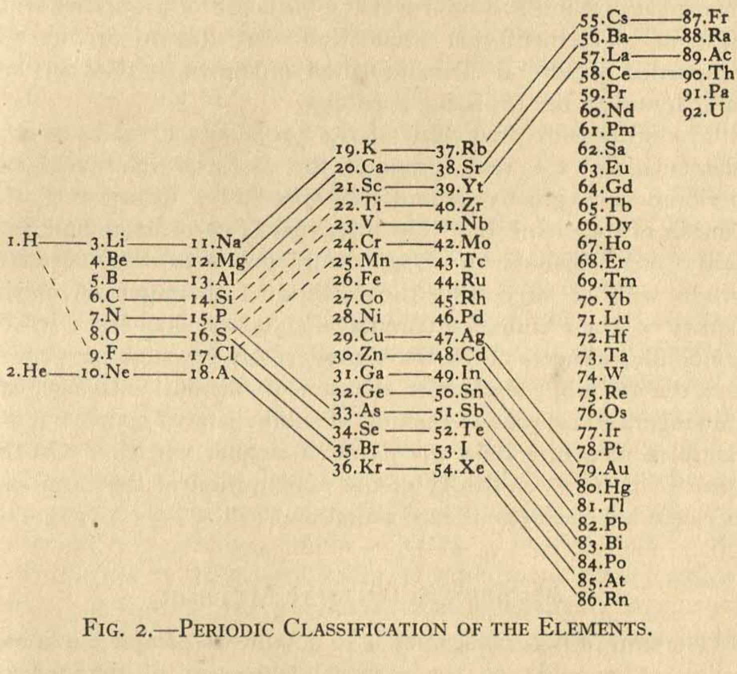


FIG. 2.—PERIODIC CLASSIFICATION OF THE ELEMENTS.

---

[1] Argon is placed before potassium, although the latter has the smaller atomic weight. This is one of the anomalies of the Mendeléeff periodic classification, and will receive its explanation later.

eighteen elements from rubidium to xenon, and then there is a jump to a still longer period of thirty-two elements, from caesium to radon. A fragmentary period of six elements completes the table.[1] Owing to the periodicity of properties, elements of similar or analogous character (*e.g.* Li, Na, K, Rb, Cs; F, Cl, Br, I) fall into corresponding places in the various periods; and, in the diagram, the members of these 'natural families' or groups of related elements are joined together by full drawn lines. Dotted lines join elements which are less closely related than are the members of the 'natural families.'

The periodic law has proved a most valuable guide in chemical investigation, and so uniform is the variation of properties from element to element that Mendeléeff was able to predict the properties of several elements, then unknown, with what was later found to be surprising accuracy.

The successful prediction of the properties of undiscovered elements and the recognition of the essential validity of the periodic law greatly stimulated speculation concerning the genesis of the elements. 'The discovery of co-ordinate families,' said Lord Salisbury in 1894, 'dimly points to some identical origin without suggesting the method of their genesis or the nature of their common parentage.' As we shall learn in the concluding chapter of this book, modern investigation has proved that the atom of the chemist, the unit of chemical exchange, can no longer be regarded as the unit of subdivision of matter but is a complex structure built up of much smaller particles. On the basis of this newer theory of the constitution of the atom, the periodic law receives its interpretation.

MODERN SCIENTIFIC METHOD

The aim of natural science is to acquire as complete a knowledge as possible of the material universe; of the objects, materials and phenomena, and the relations between the phenomena which make themselves known to us by means of the senses. The first step in the building up of this knowledge by the scientific method is to ascertain the facts, as fully and accurately as possible, by observation and experiment. This is by no means a simple matter. Knowledge and experience are required in devising the experiments, and manipulative skill and expertness are necessary for carrying them out. All measurements, moreover, are subject to experimental error; our senses, also, may deceive us and truth may be distorted by imagination or by an emotional bias. Great honesty of mind, therefore, as well as experimental skill, is needed for the accurate ascertainment of the facts of science. The study and practical pursuit of science inculcate veracity of thought and action, and this characteristic of the scientific mood may be held up as an inspiration to the community.

---

[1] The elements which have been produced artificially (p. 8) and which would follow uranium, have been omitted from the table.

The collecting of facts, however, is only the first step in the advance of science, for the object of science is not merely to collect facts but also to satisfy an intellectual desire. The man of science seeks not only to observe the phenomena of nature, but also to understand them; to see the facts not as separate, independent entities, but as parts of a larger whole. Thus, Robert Boyle subjected a certain amount of a gas (air) to a series of pressures and at each pressure measured the volume of the air. A number of separate facts were thus collected, and Boyle then went on to enquire what relation exists between the different pressures and volumes of gas. He found that when the pressure was doubled, the volume of the gas was halved, or, more generally, he could state that *the volume of a gas is inversely proportional to the pressure* (Boyle's law). This generalization or generalized statement of observed facts is called a *scientific law* or *law of nature*. Such a law, it should be emphasized, merely summarizes in a general statement or formula, a relationship which has been observed in a certain number of cases. The enunciation of a scientific law by the generalization of experimentally determined facts—the arguing from particular cases to a general or universal relation—is called *induction*. It forms the second stage in the building up of the scientific edifice.

The method of science, however, does not consist merely in the 'ordering of nature' in descriptive laws. It seeks also to correlate or 'explain' the laws; and so, with the general laws as a starting-point, scientific imagination is called upon to frame an *hypothesis* or conception regarding the fundamental nature of things. This hypothesis must, of course, be in harmony with all the facts already known and it must be such that the general laws, obtained inductively from experiment, follow as necessary consequences from the hypothesis. When the *deductions* from the hypothesis are found to be in harmony with the inductively derived laws, the hypothesis takes rank as a *theory*.

An hypothesis or theory makes it possible not only to co-ordinate or correlate the various known laws—to explain these laws, as one says—but also to predict new and undreamt of laws. It not only gives satisfaction to the mind by producing coherence and order among diverse phenomena, but it opens up vistas of new knowledge, suggests new tests of its own validity and spurs one on to fresh endeavour. Before the new laws obtained deductively from an hypothesis or theory are accepted, however, *they must be subjected to verification by experiment*. With the continual necessity, therefore, of experimental investigation and testing of deductions from theory, it will readily be understood that

> "Science moves, but slowly slowly, creeping on from point to point":

and the building up of the edifice of science is a slow and laborious task.

In approaching the study of any branch of science, and not least of chemistry, one must not think of it as a definite body of facts, laws and theories; as knowledge complete and finished, as the last word to be said. On the contrary, as knowledge advances, the horizon recedes; and the great theories of science by which one seeks to interpret nature and which stand out as among the greatest creative achievements of the human mind are, after all, somewhat tentative and provisional, and as knowledge increases, theories may have to be modified or discarded. Science must rather be thought of as something vital and growing, and its pursuit is to be regarded as a great adventure in discovery and a quest of truth in which all can take, if not an active part, at least a lively and intelligent interest.

Chapter 2

THE GASES OF THE ATMOSPHERE

SINCE modern chemistry has its roots in the explanation of the phenomenon of combustion in air (p. 35), we may well begin our consideration of the service which chemistry has rendered to man by a study of the composition and nature of the atmosphere.

The composite nature of atmospheric air, which from earliest times had been regarded as an element, was first demonstrated, in 1674, by the English physician, JOHN MAYOW, who showed that when a substance is burned in air enclosed in a vessel standing over water, the volume of the air is diminished, and that in the residual gas combustion will no longer take place. Subsequent investigations, belonging in some cases to comparatively recent times, have shown that atmospheric air is a mixture of a number of different gases in proportions which remain remarkably constant. The gases normally present in air are: nitrogen, oxygen, carbon dioxide, water vapour, and a group of gases known as the rare or inert gases, the most abundant of which is argon. Besides these normal constituents, other gases and also solid particles, derived from local sources, may be present as impurities.

As the result of analysis it has been found that the average composition of purified air, free from carbon dioxide and water vapour, is as follows:

	Per cent. by volume	*Per cent. by weight*
Nitrogen . . .	78·06	75·5
Oxygen . . .	21·00	23·2
Rare gases . . .	0·94	1·3

Nearly four-fifths of the air, by volume, therefore, consists of nitrogen, and one-fifth of oxygen. Normally, there are about three parts of carbon dioxide in ten thousand parts of air by volume.

Nitrogen was first obtained, in 1772, by a botanist, DANIEL RUTHERFORD, who burned phosphorus in a vessel containing air, and so removed, as is now known, the oxygen which was present. Very large quantities of nitrogen are now obtained industrially by the distillation of liquid air (p. 31). Although it plays a very important rôle in the economy of nature, nitrogen is a very inert or chemically inactive element at the ordinary temperature, and supports neither combustion nor life.

The discovery of *oxygen*, first announced in 1775, we owe to CARL WILHELM SCHEELE, a Swedish apothecary and one of the foremost chemists of his time, and to JOSEPH PRIESTLEY, an English Unitarian Minister, an amateur of science and one of the most versatile and intellectually active men of the eighteenth century. Both these men obtained oxygen by the decomposition by heat of red oxide of mercury, a compound of mercury and oxygen; but the gas is now best prepared on a small scale by heating a mixture of potassium chlorate and manganese dioxide. On an industrial scale, the gas is produced mainly by the distillation of liquid air, but a certain amount is also obtained by a process of electrolysis which will be discussed in *Chap.* 10.

The most conspicuous property of oxygen is the readiness with which it combines with other substances, as shown, for example, in the vigour with which it supports combustion. A merely glowing strip of wood bursts into flame when introduced into oxygen, and phosphorus burns in the gas with dazzling brightness. At the present time, oxygen finds extensive application not only in medicine, in cases of difficult breathing, but also in industry for the production of high temperatures by means of the oxy-hydrogen blowpipe (p. 67) and the oxy-acetylene blowpipe (p. 70).

Carbon dioxide, which is normally present in air only in very small amounts, may escape in considerable quantity through fissures in the earth in volcanic regions, as in the Poison Valley of Java. It occurs also dissolved in many mineral waters, from which it may escape with effervescence. Artificial aerated waters are produced by dissolving carbon dioxide in water under pressure. On a small scale the gas can be obtained by the action of an acid on chalk, soda or other carbonate. It is one and a half times heavier than air. Carbon dioxide is formed in large quantity in many natural and industrial processes, as when coal burns and when limestone or chalk is heated for the production of quicklime. It is also formed abundantly in the process of fermentation for the production of alcohol.

Owing to the fact that carbon dioxide does not support combustion, it is used to extinguish fires. Some portable fire-extinguishers are filled with a solution of sodium bicarbonate and contain also a quantity of acid in a glass tube which can be broken by means of a plunger. By the action of the acid on the bicarbonate of soda, carbon dioxide is formed and partly dissolves in the water. On opening the nozzle, the solution of carbon dioxide is ejected by the pressure of the gas. The effectiveness of the arrangement can be increased, as in the Foamite Firefoam apparatus, by adding to the liquid in the extinguisher, glue, liquorice or some other material which is capable of forming a foam or froth. When the mixture is ejected from the apparatus, a stiff foam, containing carbon dioxide, is produced, which effectively 'blankets' or smothers the fire. In the 'Firefoam' apparatus the carbon dioxide is produced, not by the action of an acid, but by the action of a solution of aluminium sulphate on sodium bicarbonate (Plates 4 and 5).

When carbon dioxide is passed into lime water (a solution of slaked lime or calcium hydroxide in water), a turbidity is produced owing to the fact that the gas reacts with the calcium hydroxide and forms insoluble calcium carbonate. This is clearly represented by the *chemical equation*:

$$\underset{\substack{\text{Calcium}\\ \text{hydroxide}}}{Ca(OH)_2} + \underset{\substack{\text{Carbon}\\ \text{dioxide}}}{CO_2} = \underset{\substack{\text{Calcium}\\ \text{carbonate}}}{CaCO_3} + \underset{\text{Water}}{H_2O}$$

This reaction is used as a *test* for carbon dioxide.

Carbon dioxide can easily be liquefied, and the liquid is placed on the market in steel cylinders. On allowing the liquid to be discharged through a nozzle into a cloth bag, or, on the industrial scale, into a high tower, rapid evaporation of the liquid takes place and the temperature is thereby lowered to such an extent that the liquid spray freezes to a snow-like solid. This solid passes into gas without melting and gives a temperature of -79° C.

(−110·2° F.).[1] It is therefore largely used as a refrigerant, *e.g.* in the manufacture of ice-cream. Owing to the fact that the solid carbon dioxide is surrounded by a layer of gas, the solid may, notwithstanding its very low temperature, be lightly placed in contact with the skin without any harm resulting. If, however, the carbon dioxide snow is pressed against the skin, painful 'burns' will be produced and the skin destroyed. Carbon dioxide snow is also used, instead of ice, in railway refrigerator cars, blocks of compressed solid carbon dioxide being placed on the floor of the car. The cold heavy gas, which is formed by sublimation, gradually rises, fills the whole car and overflows through vents at the top. Carbon dioxide snow—'drikold' or 'dry ice' as it is sometimes called—is found to be as effective as more than ten times its weight of ordinary ice.

Liquid carbon dioxide is also used in blasting operations, *e.g.* in coal-mining, where there is risk of explosion from gas or coal dust. The liquid carbon dioxide is contained in a strong steel tube from the end of which, by a special firing device, it can be rapidly discharged. The expanded gas, five hundred to six hundred times greater in volume than the original liquid, exercises a powerful heaving force and breaks down the surrounding coal or rock.

Since continually oxygen is being removed from and carbon dioxide is being poured into the air through the respiration of animals, the combustion of coal and other fuels, processes of fermentation and other industrial operations, the question arises: How does nature achieve the degree of constancy in the composition of the air which is so remarkable?

Early in the nineteenth century, the Swiss chemist, Théodore de Saussure, showed that carbon dioxide and water vapour are taken up from the air by the green leaves of plants. There, through the radiant energy of sunlight and in the presence of chlorophyll, the green colouring matter in the leaves, they are built up, step by step, into various complex compounds, such

---

[1] In scientific work, temperature is always measured on the Centigrade scale. On this scale, the melting-point of ice is represented by 0°, and the boiling-point of water by 100°. On the Fahrenheit scale, the corresponding temperatures are 32° and 212°. For the conversion of temperature on the Centigrade scale to temperature on the Fahrenheit scale, one can make use of the formula:

$$t°\text{F.} = \frac{t°\text{C.} \times 9}{5} + 32.$$

as sugar, starch and cellulose.[1] During this process, moreover, there is set free and given up to the air a quantity of oxygen, which comes entirely from the water vapour, equal in volume to the carbon dioxide removed. The green vegetation on the earth's surface, therefore, plays a very important part in maintaining the constancy of composition of the air. Large quantities of carbon dioxide, also, are removed from the air by solution in rain and in the water of rivers, lakes and oceans.

It is an interesting and impressive thought that not only growing plants but also all living animals, directly or indirectly, obtain the carbon necessary for the building up of their tissues—cellulose, proteins, carbohydrates, fats, etc.—from the carbon dioxide in the air. This also is the source, in the long-distant past, of the carbon compounds which make up our reserves of coal and petroleum; of the carbon in the great masses of limestone, chalk, coral and other forms of calcium carbonate occurring in nature; and the source also of the numerous carbon compounds produced synthetically by chemists.

The RARE GASES of the atmosphere, under which name are included helium, neon, argon, krypton and xenon, form a group of related elements, the discovery of which is one of the most romantic episodes in the history of chemistry.

In 1785, HENRY CAVENDISH, grandson of the 2nd Duke of Devonshire, a man noted for his great ability no less than for his extreme shyness and 'singular love of solitariness,' described before the Royal Society in London experiments which are at the very root of the discovery of the rare gases. Cavendish showed that when electric sparks are passed through air, combination of nitrogen and oxygen takes place; and if a solution of potash is present in the vessel of air, nitre or saltpetre (potassium nitrate) is formed. By adding further quantities of oxygen and continuing to pass the sparks, the nitrogen could be removed, and any excess of oxygen could be absorbed by a solution of *liver of sulphur* (potassium sulphide). As a result of his experiments, however, Cavendish found that no matter how long the passage of electric sparks was continued, there always remained a small bubble of gas, equal to about 1 per cent. of the air taken, which did not combine with the oxygen. Little dreaming that in that bubble of gas five hitherto unknown elements were contained, chemists assumed that the gas was only nitrogen; and for over a hundred years the importance of Cavendish's experiment was overlooked, and the little bubble of gas, so big with scientific interest, was ignored. Until 1893, therefore, chemists everywhere believed that dry air, freed from incidental impurities, consisted solely of oxygen (21·0 per cent.) and nitrogen (79·0 per cent.), together with a minute amount of carbon dioxide (about 3 parts in 10,000 of air); and so confident were chemists that they knew all about the composition of the atmosphere that the announcement of the discovery of a new element in the air, made by Lord RAYLEIGH (3rd Baron Rayleigh) and Sir WILLIAM RAMSAY at the Oxford meeting of the British Association in 1894, was received with incredulity. The story of that discovery is the story of skilful and accurate experiment, and of clear and logical reasoning.

---

[1] Chemists have now, through their investigations, gained an insight into the complex series of chemical changes, each brought about under the influence of enzyme action (*Chap.* 15), which take place in the natural production of sugar, starch and cellulose from carbon dioxide and water vapour. They have even succeeded in synthesizing some of these naturally occurring substances in the laboratory.

Lord Rayleigh, Cavendish Professor of Physics in the University of Cambridge, while engaged in the accurate determination of the density of different gases, found that 'atmospheric nitrogen,' or the gas left after removal of the oxygen from the air, had a somewhat greater density than nitrogen obtained from one of its compounds. The difference was not great, being only about 1 part in 230, but it was much greater than the possible errors of determination. Lord Rayleigh announced his results early in 1893, and invited the help of chemists in explaining the discrepancy. With the permission of Lord Rayleigh, Sir William Ramsay[1] joined in the investigation and, making use of the fact that magnesium combines with nitrogen to form a nitride, Ramsay passed 'atmospheric nitrogen' repeatedly over a red-hot mixture of magnesium and quicklime, and obtained a small quantity of residual gas which did not combine with the metal. Lord Rayleigh, also, repeated the experiment of Cavendish, but on a much larger scale, and instead of a small bubble he obtained no less than two litres[2] of gas which did not combine with oxygen.

---

[1] Perhaps the most brilliant of British chemists since the time of Sir Humphry Davy. Born at Glasgow in 1852, he became Professor of Chemistry at University College, London (1887–1912), and was awarded the Nobel Prize for Chemistry in 1904. He died in 1916.

[2] A litre or 1000 cubic centimetres (c.c.) is equal to 1·76 imperial pints.

The density of the residual gas obtained by Ramsay and by Lord Rayleigh was found to be about 20, compared with the value of 14 for nitrogen. The gas was subjected to chemical and physical treatment of every imaginable kind, but it underwent no change; and attempts to cause it to combine with other substances were entirely unsuccessful. It was a quite inactive and inert element, the first such element to be discovered, and it received, in consequence, the name *argon* (from the Greek word *argos* = inert). Since atoms of argon can exist in the free state, the molecule of argon is the same as the atom. Argon is said to be monatomic.

ARGON, which forms rather less than one per cent. of air by volume, was, for a number of years, of purely scientific interest. Now, however, it is produced in large amount from liquid air and finds important industrial application for filling incandescent electric lamp bulbs. Owing to the presence of the gas, the tungsten filament of the lamp can be heated to a much higher temperature, and a brighter light can therefore be obtained, without dispersion of the metal and blackening of the bulb taking place. In the argon arc process, also, for welding aluminium and aluminium alloys, the electric current passes through a tungsten electrode in an atmosphere of argon.

When an electric discharge is passed through a mixture of argon and mercury vapour contained, under reduced pressure, in a glass tube, a bright blue light is emitted. This fact is made use of for the production of illuminated signs.

The light emitted by incandescent mercury vapour is very rich in ultraviolet light, or light of shorter wave-length than can be seen by the eye. If, therefore, the inside of the tube is coated with certain substances, *e.g.* cadmium chlorophosphate, zinc beryllium silicate, magnesium tungstate, these substances fluoresce and become highly luminescent under the action of the ultraviolet rays. The light emitted may vary from red to blue, depending on the nature of the fluorescent material; and by coating the tubes with suitable substances, *e.g* calcium chlorofluorophosphate, a brilliant light, with a quality resembling daylight, can be obtained. This method of illumination is now being extensively used, especially for the lighting of large spaces. In place of argon, neon (p. 30) is also used to start the electric discharge.

For the identification of the rare gases, all of which are chemically quite inert, use is made of the spectroscope. When white light from an incandescent solid body is allowed to pass through a prism, it is found that the light is drawn out into a rainbow band of colour, known as a *spectrum.* In the case of the light emitted by an incandescent gas, however, the spectrum consists not of a continuous band, but of isolated lines of colour, each line occupying a certain definite position and corresponding to light of a certain definite wave-length. Since each gas gives its own characteristic spectrum or arrangement of lines, it is easy, by determining the position of the lines with the aid of a spectroscope, to identify a gas.

In 1868, the French astronomer, Professor P. J. C. JANSSEN, and the English astronomer, Sir NORMAN LOCKYER, while examining the spectrum of the sun's chromosphere during an eclipse, observed a yellow line which they could not find in the spectrum of any known terrestrial substance. Lockyer, therefore, concluded that it must be due to some extra-terrestrial element to which he gave the name of HELIUM (from *hēlios*, the Greek word for sun). The element remained unknown on the earth until the year 1895, the year after the discovery of argon, when it was isolated by RAMSAY from the uranium-containing mineral, cleveite.

On examining the spectrum of the gas given off by this mineral on treatment with acid, Ramsay at once realized that the gas was neither nitrogen nor argon; and Sir WILLIAM CROOKES, to whom the gas was submitted for spectroscopic examination, at once pronounced it to be none other than the helium of Lockyer and Janssen.

Behind this discovery lies one of the tragedies of scientific investigation, for, even in 1890, the evolution of a gas when cleveite is treated with sulphuric acid, had been observed by W. F. Hillebrand, of the U.S. Geological Survey, but the gas was supposed to be nitrogen. For Hillebrand, the investigation of the gas lay outside his proper work and, although he had observed in the spectrum of the gas certain lines which he could not identify, he rejected a suggestion, 'made in a doubtfully serious spirit,' that a new element might be in question. And so, through not following up a clue, Hillebrand failed to discover helium, just as Cavendish failed to discover argon.

Investigation of this new gas showed that it is an element with the atomic weight 4·00, and that, like argon, it is chemically inert and incapable of forming any compounds. As in the case of argon, also, the molecule consists of only one atom. It is the most difficult of all gases to liquefy, and the liquid boils, under atmospheric pressure, at a temperature of −268·7° C. (−515·7° F.).

Helium is now known as a disintegration product (alpha rays) of radioactive substances (*Chap.* 17), and it is consequently found in most radioactive minerals. It has also been found in certain naturally-occurring waters, *e.g.* in the mineral springs of Bath, and it occurs in air to the extent of about 1 part in 200,000 by volume. The main source from which it is obtained, however, is the natural gas which escapes from the earth in certain parts of the world, more especially in the State of Texas, in North America, where many millions of cubic feet of helium are produced annually.

The natural gas, which comes to the separation building under a pressure of 650 lbs. per square inch, is cooled and allowed to expand. The lowering of temperature which is thereby produced serves to liquefy most of the natural gas, whereas the helium is collected in the gaseous form. The natural gas, freed from helium, is used over a very wide area for heating and illuminating purposes.

Helium is used in U.S.A. for filling balloons, and for this purpose it possesses the great advantage over hydrogen of not being inflammable. Although the density of helium is twice that of hydrogen, its lifting power is not much less, because the lifting power depends only on the difference between the density of the air and that of the gas. Taking the densities of hydrogen, helium and air as 1, 2 and 14·4 respectively, the lifting power of hydrogen and of helium will be as 13·4 is to 12·4. That is to say, the lifting power of helium is 92·5 per cent. of the lifting power of hydrogen.

Helium also finds use in the treatment of respiratory diseases and for the production of artificial breathing atmospheres for caisson workers and divers working at great depths. If, in these cases, divers are supplied with ordinary air, nitrogen dissolves in considerable quantities in the blood under the existing high pressure; and the dissolved nitrogen induces a narcotic effect which lowers the diver's efficiency. This narcotic effect is avoided by supplying the diver with an atmosphere of oxygen and helium. Moreover, when the diver is brought to the surface, the period of gradual decompression which is necessary to prevent the too rapid escape of dissolved gas from the blood can generally be reduced when an atmosphere containing helium in place of nitrogen is used.

Under the influence of an electric discharge, helium emits a pale yellow light, and is used in the construction of illuminated signs.

Owing to the discovery of the monatomic elements, argon and helium, which are chemically inert and may therefore be regarded as having no combining power or as having zero valency, a new family of elements had to be inserted in the periodic classification of Mendeléeff. Since, moreover, helium preceded the metallic element lithium, and argon the element potassium, it seemed probable that other similar elements would exist and take their places in front of the elements sodium, rubidium and caesium (Fig. 2, p. 17). In 1896, therefore, a systematic search for the missing elements was commenced by Sir William Ramsay and Morris W. Travers, and was pursued with such energy and ability that in a short time three new elements were obtained from the air, namely, *neon*, *krypton* and *xenon*. The identity of these gases was established by means of the characteristic spectra which they give; and the determination of their atomic weights showed that they were the elements sought for. In the space of a few years, therefore, no fewer than five new elements, present in the air, were discovered; and the series of the rare gases was completed some years later by the discovery of radon, the radioactive gas or 'emanation' given off by radium (*Chap.* 17).

Besides helium and argon, neon, which occurs in the air to the extent of only fifteen parts per million, has already found practical application for filling 'Osglim' lamps (night lights and emergency lights), for lamps used as beacons at airports, and in the construction of illuminated signs. Under the influence of the electric discharge, the gas glows with a brilliant rose colour.

Krypton and xenon are used in place of argon for filling electric lamp bulbs, especially those for use in miners' lamps. Such lamps are much more efficient than those containing argon. A xenon-filled gas arc lamp has also been produced which emits a very bright light. It is used for signalling, for flashlight photography and for film projection.

Although krypton and xenon are present in the air to the extent of only one part per million and one part per eleven million parts of air respectively, they are now commercial materials.

The discovery and isolation of five hitherto unknown elements is one of the great epics in the history of chemistry; and no one who lived through the years when the discovery, in rapid succession, of new gas after new gas, new element after new element, was announced to the world could fail to feel a thrill of wonder which impelled one to exclaim, with Keats:

> Then felt I like some watcher of the skies
>   When a new planet swims into his ken;
> Or like stout Cortez when with eagle eyes
>   He stared at the Pacific—and all his men
> Look'd at each other with a wild surmise—
>   Silent upon a peak in Darien.

Nitrogen, oxygen and the inert gases (except helium) are obtained industrially by the fractional distillation of liquid air, the production of which is now a very simple matter. The principle on which the process of liquefaction depends is that when compressed air is allowed to expand rapidly, its temperature falls; and the amount by which the temperature falls is all the greater the lower the temperature of the air before expansion.

Air, therefore, under a pressure of 150–200 atmospheres is allowed to expand at a valve, and the expanded and cooled air is caused to lower the temperature of the compressed air passing towards the expansion valve. In this way, the air expanding at the valve becomes progressively colder until a point is reached at which the lowering of temperature on expansion is so great that the air liquefies.

The utilization and preservation of liquid air were greatly facilitated by the introduction by Sir JAMES DEWAR, Professor of Chemistry at the Royal Institution, London, of 'vacuum vessels,' now so familiar under the name of 'thermos' flasks. These consist of double-walled

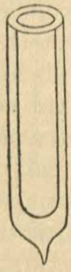


FIG. 3.—DEWAR VACUUM VESSEL

glass vessels (Fig. 3) from the space between the walls of which the air is removed as completely as possible. The 'vacuum' thus obtained acts as a very efficient heat insulator, and the efficiency of the insulation can be increased by silvering the inner walls of the vessel. By this means the passage of radiant heat can to a great extent be prevented.

INSTITUTE OF EDUCATION FOR WOMEN ★ CALCUTTA-27 ★
Dept. of Extension
SERVICE.

Chapter 3

COMBUSTION AND THE PRODUCTION OF FIRE

ONE of the most typical, most familiar and most important cases of chemical action is that which is observed in the process of combustion or the burning of substances in air. The manner in which the first visible combustion, or fire, was brought about on the earth will doubtless always remain unknown. It may, perhaps, have had its origin in some lightning flash, or in the sparks struck from the flints of primitive man; or it may have been produced by the self-heating of combustible material, or by the rubbing together of dried wood; or it may be that, as in the *Song of Hiawatha*:

> Gitche Manito, the mighty,
>
> . . . . .
>
> Breathed upon the neighbouring forest,
> Made its great boughs chafe together,
> Till in flame they burst and kindled.

But in whatever way fire was first produced, its importance and value were early recognized, as one can understand from the sanctity with which all primitive peoples have endowed the hearth; from the Promethean legend of a boon stolen from, not granted by, the gods; as well as from the later belief of the followers of Zoroaster, that fire is the special abode of divinity.

And even in modern times, although the feeling of reverence or of awe is no longer inspired by a process which can be explained in terms of chemical action, and can be produced at will by the striking of a match, one is not likely to underrate the importance of combustion when it is remembered that our present-day civilization in all its manifold forms of expression, in manufactures, in railway and steamship transport, in artificial illumination, etc., is based, to a large extent, on a process of combustion.

What then is the explanation of this process of combustion?

Not so very long ago the view was held that the property of combustibility was due to the presence in the combustible substance of a fiery principle, *phlogiston*;[1] and that when a substance burns, the phlogiston escapes, leaving behind the ash, or calx, as it was called in the case of a metal. Charcoal, which burns leaving practically no ash, was therefore regarded as being almost pure phlogiston. This was the explanation of combustion given, more especially, by the German chemist, STAHL, towards the end of the seventeenth century; and it was not till a hundred years later that the 'phlogiston theory' was finally overthrown by LAVOISIER,[2] who died in 1794, a victim of the guillotine, in the troublous times of the French Revolution (Plate 6).

The long life of such an erroneous theory as that due to Stahl may be attributed to the fact that chemistry was, at that time, still largely a qualitative or descriptive science, and it was considered that form rather than weight was the characteristic property of substances. The balance, of course, was known and used, but its importance was not fully appreciated; so that when it was found that the products of a combustion weigh more than the original combustible substance, the upholders of the phlogiston theory sought to defend their position by identifying phlogiston with the 'principle of levity.' The escape of the 'principle of levity' from the body left the body heavier.

Much as one may be inclined to smile at such an explanation, one ought to remember that the phlogiston theory served usefully its day and generation, and satisfied even the modern requirements of a theory, in that it gave an explanation of combustion which satisfied men's minds at the time, and also inspired a large amount of fruitful investigation. Who can say that even some of our most cherished theories may not be considered by the unthinking a hundred years hence to be equally worthy of derision? The phlogiston theory, however, long outlived its usefulness, and the tenacity with which it maintained itself is an instructive illustration of the difficulty which most minds have of freeing themselves from the authority of a long-held theory ; and it conveys a lesson, which is not unnecessary even at the present day, that a theory from being a helpful guide may readily become an oppressive tyrant. As LIEBIG wrote many years ago, after having himself been a victim of the misfortune to which he refers: 'No greater misfortune could befall a chemist than that of being unable to shake himself free from the power of preconceived ideas, and, yielding to the bias of his mind, of seeking to account for all phenomena which do not fit in with these ideas by explanations which have no basis in experiment.'

---

[1] The word is derived from the Greek verb *phlogizein*, meaning to burn.

[2] Antoine Laurent Lavoisier, the most brilliant of the French chemists of the eighteenth century, was born in Paris in 1743, and made many contributions of the greatest importance to chemistry. He became a member of the *Ferme Générale*, was denounced by Marat as acting contrary to the commonweal, and was beheaded on 8th May 1794.

The irresistible force of facts, however, was gradually increasing, and after the discovery of the gas oxygen by Priestley and by Scheele, about the year 1774, Lavoisier was able to put forward a new interpretation of the process of combustion of substances in air; and with that interpretation, modern chemistry was born.

It was known that air consists of two parts or constituents, an 'active' part which enables a substance to burn and an 'inactive' part (nitrogen), in which combustion does not take place. During a visit to Paris in 1774, Priestley, while dining one day with Lavoisier, mentioned his discovery of a gas, now known as oxygen (p. 22), in which a candle burned much better than in common air. Lavoisier at once conceived the idea that this new gas represents the portion of the air which combines with a metal and gives rise to the calx; and the explanation of combustion was thus to be found in the chemical combination of the burning substance with the oxygen of the air. The correctness of this idea was proved by quantitative experiment and the actual weighing of the substances.[1]

The calx of mercury (now known as oxide of mercury) was first produced by heating a weighed amount of mercury in a retort which communicated with a known volume of air contained in a bell-jar standing over mercury (Fig. 4). The mercury in the retort was heated on a charcoal furnace for twelve days at a temperature just below its boiling-point. At the end of this time a quantity of the red calx of mercury, 45 grains in all, had formed on the surface of the metal, and the volume of the air in the bell-jar had diminished by 7–8 cubic inches. The residual gas in the bell-jar did not support life or combustion.

---

[1] It may, perhaps, be remarked in passing that it was Lavoisier who, owing to the constant use which he made of the balance and the importance which he attached to its indications, established the fundamental law of physical science, the *law of the conservation of matter* or *conservation of mass*, which states that in no chemical action is matter either created or destroyed; the sum of the masses of the reacting substances is equal to the sum of the masses of the products formed. The matter can be changed in form; it cannot be altered in quantity. Although in the case of ordinary chemical reactions one may still accept the law of conservation of matter, it is necessary in other cases to combine the law of conservation of mass with the law of conservation of energy (*Chap.* 17).

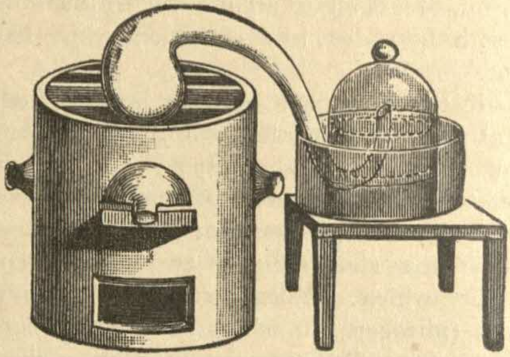


FIG. 4.—LAVOISIER'S EXPERIMENT OF HEATING MERCURY IN AIR

The red calx of mercury was then heated to a higher temperature, and Lavoisier found that from 45 grains of the calx, 41 grains of metallic mercury were formed and 7–8 cubic inches of a gas (oxygen) were evolved.

It was thus shown by Lavoisier that when a metal or other substance is burned in air, the oxygen of the air combines with the metal or burning substance. In other words, *the process of combustion is a chemical reaction between the burning substance and the oxygen of the air, the process being accompanied by emission of heat and, it may be, light.* A flame, however, is formed only when the burning substance is a gas at the temperature of the combustion. The nitrogen of the air takes no part in the process, but acts merely as a diluent which moderates the vigour of the combustion.

Since combustion in air is due to a chemical reaction between the burning material and oxygen, a process which is known as *oxidation*, the vigour of combustion can be increased by increasing the rate at which oxygen is supplied to the burning material; and this is what one does when one blows a fire with a bellows. Conversely, combustion can be stopped by preventing access of oxygen to the burning material, as happens when one uses, for example, the Foamite fire extinguisher (p. 23). Similarly, the Pyrene fire extinguisher, largely used on motor cars, is filled with a liquid, carbon tetrachloride, which when squirted on burning material forms a heavy vapour. This vapour effectually 'blankets' the fire and prevents access of atmospheric oxygen to the burning material.

If the explanation of combustion which has just been given is correct, the question arises: Why does a combustible material not take fire when it is exposed to the air? Coal gas, for example, may be allowed to escape from the burner, or a candle or piece of wood or coal may be left exposed to the air, or even to pure oxygen, without any apparent change taking place; and in order that they shall exhibit the phenomenon of combustion, that is, in order that they shall undergo the process of oxidation, or combination with oxygen, with production of heat and light, it is necessary to heat the materials up to a certain temperature, called the *ignition-point.* Combustion then goes on of itself. The explanation of this fact is that the velocity or vigour of every chemical change is increased by raising the temperature. At the ordinary temperature, the oxidation of the candle or the coal takes place so slowly that no change is apparent even over long periods of time. If, however, the temperature of the combustible material is raised, the rate at which it reacts with the oxygen of the air rapidly increases, and consequently the production of heat which accompanies the reaction also rapidly increases, and the temperature rises progressively. When this reaches a certain point, the ignition-point, the reaction takes place with such rapidity that the heat which is produced by the process of oxidation is sufficient to raise the substances to incandescence and also to maintain the burning substance at a temperature above the ignition-point. The process of combustion is thus enabled to proceed continuously.

On the other hand, if the burning substance is cooled sufficiently, the temperature is lowered to below the ignition-point, and so the combustion ceases. A simple experiment which can be carried out by anyone will serve to demonstrate this important truth. If a piece of metal wire gauze is held at a distance of half an inch or an inch above a burner from which coal gas is issuing, and if a light is then applied to the gas *above the gauze*, it will be found that the flame of burning gas is arrested by the gauze and does not pass through to the burner (Fig. 5); for the wire gauze conducts the heat of the flame away so rapidly that the temperature is lowered to below the ignition-point of the gas. Only after the gauze has become quite hot does the gas below the gauze become ignited. Similarly, if the gauze is brought down on a flame of burning gas, the flame is extinguished at the gauze. The gas itself, however, passes through, as can be shown by bringing a light to the upper surface of the gauze, when the gas will take fire.

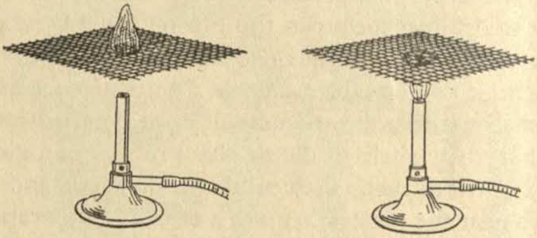


FIG. 5.—EXTINCTION OF FLAME BY WIRE GAUZE

The cooling power of wire gauze received, early last century, an application of the highest importance in the miner's safety lamp invented by Sir HUMPHRY DAVY. This lamp has undergone a marked improvement, and the modern safety lamp shows little sign of the means whereby safety is secured (Fig. 6). Careful examination, however, will show that all the holes through which air can pass to the flame, or the hot air and products of combustion can pass out, are protected by fine wire gauze. Combustible gas, therefore, can pass through this gauze and burn inside the lamp but the flame cannot pass through the gauze and be communicated to the explosive mixture of fire-damp and air in the mine.

Although electric lamps have now, to a large extent, replaced the oil safety lamps for lighting purposes, the latter are required to be used in all mines for reasons of safety. Warning of the presence of the dangerous fire-damp is given to the miner through the luminous flame of the lamp becoming crowned by a 'cap' of pale blue flame. The greater the amount of fire-damp the larger is the cap.

The process of combination with oxygen which, as we have seen, is the essential feature of the combustion process in air, may go on appreciably even at temperatures below the ignition-point. Thus, when iron is exposed to moist air, it rusts. This rust is oxide of iron, a compound of iron and oxygen; and the process of rusting is therefore a process of oxidation, a process of combustion, against which it is necessary to protect, by paint or other means, all iron structures exposed to the air, if we would have them last. The rusting of iron is said to be a process of *slow combustion*, because the temperature does not rise to the point of incandescence. Slow combustion can be demonstrated more strikingly with the metal aluminium, which combines with oxygen more vigorously than iron does. When finely divided aluminium is heated in the air, as, for example, when aluminium powder is blown through a flame, it burns with a very bright

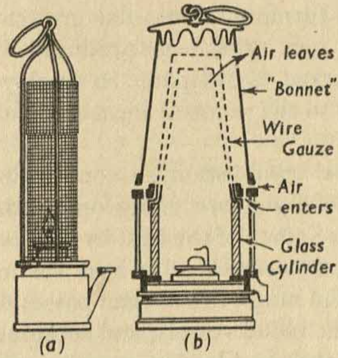


FIG. 6.—MINER'S SAFETY LAMP

In the old form of lamp, the flame was surrounded by a closed cylinder of wire gauze which considerably diminished the light emitted by the lamp; but in the modern type, a cylinder of glass is inserted, whereby the efficiency of the lamp is greatly increased.

light; but when exposed to the air at the ordinary temperature, the metal remains apparently unchanged. As a matter of fact it rapidly combines with the oxygen of the air, but the coherent film of oxide which is formed on the surface protects the metal from further attack, and therefore no change is apparent. By coating the surface of the metal with mercury, however, a liquid amalgam or alloy of mercury and aluminium is produced, and the formation of a coherent film of aluminium oxide is thereby prevented. The aluminium is consequently no longer protected from the continued action of the oxygen of the air. In this case it is observed that the aluminium undergoes oxidation quite rapidly, the oxide forming a moss-like growth on the surface of the metal. The heat which is produced by the oxidation, although quite marked, is dissipated so quickly that the temperature does not rise to the point of incandescence, and so no light is seen.

Processes of slow combustion, or combustion unaccompanied by the emission of light, are going on continually within our bodies, and are the source of the heat by means of which the temperature of the body necessary for health is maintained. When air is drawn into the lungs, the oxygen passes or diffuses through the thin walls of the blood vessels, and combines with the hæmoglobin present in the red blood corpuscles. On the other hand, carbon dioxide passes from the venous blood into the air-spaces of the lungs and is expelled in the expired air. The oxygen, in the form of oxy-hæmoglobin, is carried by the blood to all parts of the body, and oxidizes or burns the tissues and assimilated food materials with production of carbon dioxide and water, the former being then conveyed by the blood back to the lungs and so got rid of. Oxygen, then, is necessary for respiration as well as for combustion in air, and, although prolonged inhalation of pure oxygen would be harmful by producing too rapid oxidation in the body, the gas is frequently administered in cases of difficult breathing due to pneumonia or other diseases of the lungs.

The presence of carbon dioxide in expired air is readily shown by blowing through a tube into clear lime water (a solution of slaked lime in water). The liquid very speedily becomes turbid owing to the separation of insoluble carbonate of lime, formed by the combination of carbon dioxide with the slaked lime (p. 23).

In the processes of putrefaction and decay, also, we have examples of slow combustion in which animal and vegetable material is oxidized by the oxygen of the air, with the co-operation of various micro-organisms; and efficient aeration, as in a rushing and tumbling stream, is an excellent means of purifying water from all kinds of organic contamination.

Under favourable conditions, the process of slow combustion may pass into rapid combustion with production of light. For, if the heat which is produced by the combination of the oxygen with the combustible material is prevented from being dissipated, the temperature will go on rising gradually, and as the temperature rises, the vigour of the combustion, or chemical combination, increases. More and more heat, therefore, is produced in a given time, the temperature rises more and more rapidly until, finally, it reaches the ignition-point of the combustible material. The slow combustion passes into rapid combustion, and the combustible material takes fire without the application of external heat; in other words, it undergoes *spontaneous combustion.* In this way arise, for example, the so-called 'gob' fires, in spaces from which coal has been removed and where coal-dust and fine coal remain behind; so also may fire break out in coal bunkers and in other confined spaces in which combustible matter, like oily cotton waste, is stored without proper ventilation. Such spontaneous combustion will, of course, take place with special readiness in the case of readily inflammable substances, or substances which have a low ignition-point, such as phosphorus. Thus if this substance is dissolved in the liquid known as carbon disulphide, and if the solution is then poured on a sheet of filter paper, or thin blotting-paper, the carbon disulphide soon evaporates and leaves the phosphorus on the paper in a finely divided state. The oxygen of the air rapidly unites with the phosphorus, and the heat which is thereby developed soon raises the temperature to the ignition-point of the phosphorus, and rapid combustion sets in.

Although the most familiar examples of combustion are those which take place in air, the term combustion must not be restricted only to such cases. Combustion, in its widest meaning, is a process of chemical action in which so much heat is generated that the burning substance becomes incandescent and emits light; and such a process may occur even when no air or oxygen is present. Thus, for example, the gas hydrogen will burn not only in air, with production of the substance water, but it will also burn in the gas chlorine with formation of the compound known as hydrogen chloride or hydrochloric acid gas. And similarly, other cases of combustion are known which do not depend on the presence of oxygen, and are not processes of oxidation.

Even when the combustion is due to the reaction of the combustible material with oxygen, to a process of oxidation as we have called it, the oxygen need not be present in the gaseous form, but may be yielded up by some compound containing it. Various well-known substances, such as chlorate of potash (potassium chlorate), $KClO_3$, and saltpetre (potassium nitrate), KNO_3, can act as suppliers of oxygen in this way, and the use of such substances for promoting combustion has long been known. *Touchpaper*, for example, the slow-burning paper which is so familiar in connection with fireworks, is prepared by soaking paper in a solution of saltpetre and allowing it to dry. The saltpetre is in this way deposited in the fibres of the paper, and renders the latter more readily combustible. In the case of gunpowder, also, which will be discussed at a later point, saltpetre is similarly made use of as a reservoir of oxygen.

Red lead (Pb_3O_4) and hammerscale (oxide of iron, Fe_3O_4) can also be used as reservoirs of oxygen; and in the self-heating cans of soup (Fig. 7), supplied to Commandos during World War II, use was made of a mixture of calcium silicide and hammerscale. A priming mixture of calcium silicide and red lead could readily be ignited by means of a fuse and this initiated the reaction between calcium silicide and oxide of iron. The heat evolved served to warm the soup.

The process of combustion by means of combined oxygen has also been turned to very good account for the production of high temperatures and for the purpose of obtaining certain metals from their oxides. If oxide of iron is mixed with powdered aluminium and the mass strongly heated at one point by means of a special ignition mixture, the aluminium combines with the oxygen of the iron oxide; and so much heat is thereby generated that a temperature of nearly 3000° C. (about 5400° F.) is produced. This reaction, known as the alumino-thermic reaction, forms the basis of the so-called *thermit* process, a process which has become familiar through its application to the welding of tramway rails and to the repair, *in situ*, of broken castings, shafting, etc. The mixture of iron oxide and aluminium is ignited and the molten iron which is produced in the process and raised to a high temperature by the vigour of the reaction is run into a mould formed round the ends of the rails or fractured metal. The rails are thus raised to such a high temperature that they can be readily welded by pressure, or the fracture is filled with fresh iron and a solid joint effected.

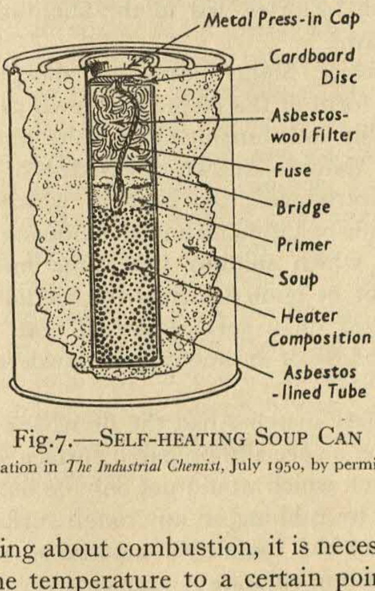


Fig.7.—Self-heating Soup Can
(Based on an illustration in *The Industrial Chemist*, July 1950, by permission of the Editor.)

In order to bring about combustion, it is necessary, as we have seen, to raise the temperature to a certain point, the ignition-point. Nowadays this causes no difficulty; and it may be regarded as, perhaps, not the least of the services which chemistry has rendered to man, that it has put it within his power to obtain fire at will, with a minimum both of trouble and expense.

One of the characteristics of chemical action, as we have seen it exemplified in the process of combustion, is the production of heat, but it was not till early in the nineteenth century that practical suggestions were made for the employment of such means of producing fire. One of the earliest forms of match consisted of a thin strip of wood tipped with a mixture of potassium chlorate and sugar bound together by means of gum. When this composition was dipped in concentrated sulphuric acid, it took fire. Other mixtures also were introduced which could be inflamed by friction.

During the nineteenth century the very readily inflammable substance, *phosphorus*, mixed with an oxygen-containing substance such as red lead, came into use for the heads of matches; and these matches, known as Congreves, were almost universally used for many years. The number of deaths, however, which took place due to phosphorus poisoning and the disease known as 'phossy jaw,' or necrosis of the jawbone, which attacked the workers in match factories, led to the abolition of the use of phosphorus by law.

Besides this white, highly poisonous phosphorus, however, there is another form of the element, known as *red phosphorus.* This is less readily inflammable than white phosphorus and is non-poisonous. Matches, known as Swedish or safety matches, were therefore introduced, the head of which consisted of a mixture of sulphide of antimony and an oxidizing substance, such as red lead, to which sulphur was sometimes added. This mixture could not be ignited merely by friction, but when the match was rubbed on a surface coated with a paste of red phosphorus, sulphide of antimony and powdered glass, it took fire.

Since these safety matches had the drawback that they could be ignited only on a specially prepared surface, chemists sought to produce a match which would not only be non-poisonous but could be ignited by rubbing on any rough surface. The 'strike anywhere' match which has a tip composed of sulphide of phosphorus and potassium chlorate is very extensively used.

Although the ordinary match is doubtless the most usual means of obtaining fire and light, more recent years have seen the introduction and greatly extended use of 'petrol lighters,' in which the vapour of petrol is ignited by sparks produced by the rubbing of a pyrophoric cerium-iron alloy against a steel wheel. In this apparatus we have, in a refined form, the flint and steel of olden days.

In these lighters, butane (p. 53) is also used in place of petrol.

Chapter 4

FUELS AND ILLUMINANTS

SOLID FUELS

UNTIL comparatively recent times, down, say, to the seventeenth century, wood was the almost universal fuel; but coal, since first it began to be mined, has become, in an ever-increasing degree, the immediate source of the energy on the utilization and transformation of which our present-day civilization depends. It now occupies a position of unquestioned pre-eminence.

Coal consists of the fossil remains of early luxuriant vegetations. Through an age-long process the cellulose, of which the woody fibre essentially consists, has become converted, through the action of bacteria and fungi and under the influence of high temperature and pressure, into more highly carbonized compounds; and the proportion of hydrogen and oxygen has diminished owing to the formation of gaseous substances such as carbon dioxide and marsh gas. From the figures given in the following table, one can recognize the gradual carbonization of cellulose, the materials peat, lignite or brown coal, bituminous coal and anthracite representing progressive stages in the natural process.[1]

	Carbon	*Hydrogen*	*Oxygen*	*Calorific value B.Th.U. per lb.*
Cellulose $(C_6H_{10}O_5)_n$	44·5	6·2	49·3	7,500
Wood (dry) . .	50·0	6·0	44·0	8,600
Peat (Irish) . .	60·0	5·9	34·1	9,900
Lignite . . .	67·0	5·2	27·8	11,700
Bituminous coal .	88·4	5·6	6·0	14,950
Welsh steam coal .	92·5	4·7	2·7	15,720
Anthracite . .	94·1	3·4	2·5	

---

[1] It must be noted that wood, peat and coal are not definite chemical compounds, and that the composition of the different kinds of coal may vary considerably. The numbers given in the table, therefore, are only approximate values representing, as it were, the composition and calorific value of an average

The process of carbonization is accompanied by a diminution of the amount of gaseous and volatile matter which the fuel can yield on being heated, and this markedly affects the manner in which the different materials burn. Dry wood, we know, burns readily and with a bright and cheerful flame, whereas anthracite, which represents the most advanced stage in the natural process of carbonization of woody fibre, is ignited only with difficulty, and burns with a very small and not strongly luminous flame.

It is not, however, the cheerfulness with which the fuel burns that concerns us here, but the all-important question of how much heat is given out in the process of combustion. It is the 'calorific value' of the fuel that claims our attention just now.

When one examines the different solid fuels from this point of view, it is found, as the figures in the last column of the table on p. 45 show, that with the progressive carbonization, the heat-producing power of the fuel increases, so that among all the solid fuels, anthracite stands pre-eminent. A British thermal unit[1] represents the amount of heat required to raise the temperature of one pound of water through 1° F., and the numbers in the table show that whereas one pound of dry wood will give out, on burning, about 8,600 units,[2] an equal weight of bituminous or household coal will yield about 14,900, while Welsh steam coal and anthracite will give 15,700 units. On this fact depends the great value of anthracite as a fuel.

Although wood is still used to some extent as a fuel, more especially in domestic heating, it cannot, on account of its price and low heat-producing power, find general adoption. The value of wood, in fact, as a material for constructional purposes and as a source of cellulose (for the manufacture of paper, rayon, etc.) and other products, is much greater than its value as a fuel.

member of the different classes. Moreover, other substances, more especially compounds of nitrogen and sulphur, are present, besides carbon, hydrogen and oxygen; but although, under certain conditions, these substances may give rise to important and sometimes undesirable by-products, their influence on the fuel-value of the combustible materials is very small.

[1] Heat energy is very frequently measured also in calories, a calorie being the amount of heat required to raise 1 gram of water through 1° C. A British thermal unit is equal to 252 calories.

[2] Under ordinary conditions the calorific value is considerably less than this owing to the presence of 15–20 per cent. of moisture.

In the great peat deposits of the world[1] there exists an enormous potential supply of fuel. For many years peat has had a local importance as a domestic fuel; and in more recent times, in Germany, Russia and other countries, it has been used on a large scale for power production. In Ireland several power-generating plants, fuelled entirely with peat, have been established. Further developments in the use of peat are possible.

When one considers the very great variations in the calorific value of different kinds of coal, it will at once be clear that it is rather irrational to buy coal merely by weight, without regard to the amount of heat which the coal can give out. The price paid should be related to the heat-producing value of the coal.

The world's supply of coal, on which our present-day industrial civilization mainly depends, is being used up incomparably more quickly than fresh coal is being formed; and the problem how most efficiently to utilize the irreplaceable coal reserves is therefore exercising the minds of the scientific leaders of industry in all countries. The problem of coal economy and coal utilization, moreover, must not be regarded merely from the point of view of the use of this mineral as a fuel or as the source of other fuels (oil or gas), for it must not be forgotten that coal, in the hands of the chemist, is also the ultimate source of very valuable chemical products—dyes, drugs, plastics, explosives, etc.—derived from the product of its distillation, coal tar. From coke and steam, moreover, a gas (water-gas) is produced which, as we shall learn later, is not only an important fuel but is also the raw material from which substances of great industrial and economic value are produced.

Whereas, in industry, the necessity for the efficient utilization of coal as a fuel is generally recognized, it must be confessed that the use of raw coal in the open domestic fire-place, so common in Great Britain, is a most wasteful method of heating. When fresh coal is put on a fire, a process of 'dry distillation' takes place with production of gas and tarry products, which, undergoing a partial decomposition with separation of carbon (soot), give rise to clouds of smoke. Thereby, it has been shown, as much as a third of the heat value of the coal is lost. With the ordinary open fire-place only about one-fifth of the heat of the burning coal becomes effective in heating the room.

---

[1] The area of peat moors in Europe has been estimated at 140,000,000 acres, and in Ireland alone the available peat has been estimated as equal to 2,500,000,000 tons of coal.

But if the open fire is wasteful, one will not willingly consent to give it up, and against its wastefulness one may place its efficiency in promoting ventilation and the hygienically advantageous manner of heating by radiation. Moreover, its comfortable appearance, 'the wee bit ingle blinkin' bonnily,' is something which has a value of its own, not recognized perhaps by science, but which doubtless reacts powerfully on the temperament and character of the people. Attempts therefore have been made to produce a fuel which can be burned in the open fire and which avoids the waste accompanying the production of smoke. By heating coal in retorts, out of contact with air, one can avoid the most wasteful part of the process of burning coal in the open fire, for the illuminating gas, ammonia and tar which are produced are collected, and the *coke* which is left behind can be used as a smokeless fuel. Although the ordinary coke of the gas-works, obtained by carbonizing coal at a temperature of about 1100° C. (about 2000° F.), is such that it cannot be burned as readily as coal in the open fire—although great advances in this direction have recently been made—it has been found that by carrying out the carbonization at a temperature of about 500° C. (about 930° F.), the residual coke still contains sufficient volatile matter to enable it to burn readily and without smoke in the ordinary grate. Considerable quantities of this low-temperature coke, having a calorific value of 13,500 B.Th.U., are now produced under various names (coalite, fuelite, etc.), and the greatly increased production and use of such a smokeless fuel calls for serious consideration.

Not only does the use of raw coal as a fuel involve the loss of by-products, but it is also accompanied by the production of much smoke by which the atmosphere is polluted and the health of the people prejudicially affected. What could be more depressing to the spirits of the people in some of our large towns than the want of sunlight and the appearance of 'the sombre houses hearsed with plumes of smoke'? In some industrial areas it has been shown that the available sunlight, the great minister of health, is reduced by as much as 40 per cent., owing to the presence of smoke in the air; and no less than 400–500 tons of soot fall per square mile per annum.

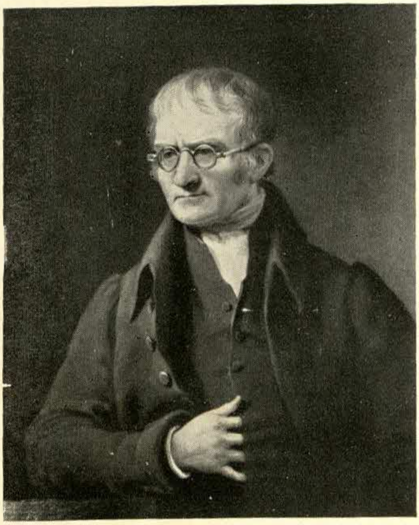
1. THE ALCHEMIST

After a painting by A. van Ostade (1661)

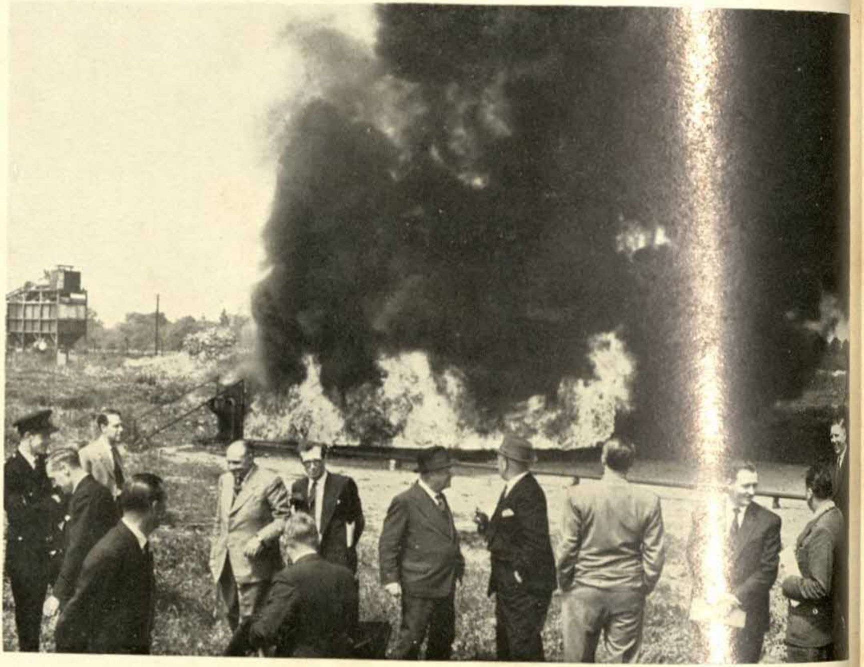
On the sheet of paper lying on the floor, the artist, with ironic humour, has painted the words, *oleum et operam perdis*—thou labourest in vain

2. ROBERT BOYLE

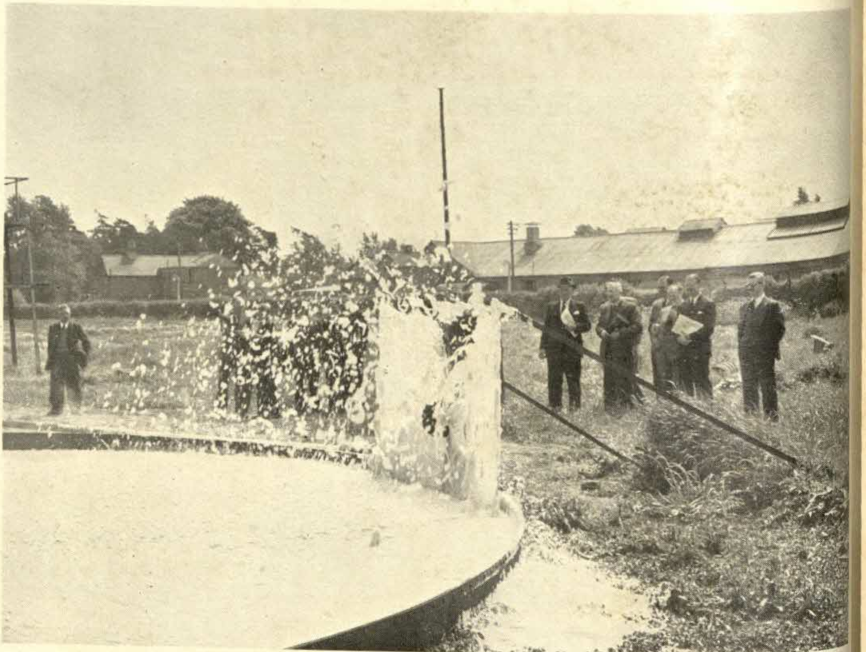
From the painting after F. Kerseboom



3. JOHN DALTON



4. FIRE OF BURNING OIL



5. OIL FIRE EXTINGUISHED BY FOAMITE FIREFOAM

Besides the lowering of vitality and the predisposition to disease brought about by a smoky atmosphere and absence of sunlight, great material damage is also done, and great monetary loss is caused owing to the increased cost of cleaning and larger laundry bills. It is, therefore, highly desirable that, to an ever-increasing extent, smokeless fuels shall replace raw coal in the domestic fire-place. The poet will then no longer be able to exclaim:

> Look ! where round the wide horizon
> Many a million-peopled city
> Vomits smoke in the bright air.

Coal contains small quantities of compounds of sulphur, and when the coal is burned an acid oxide of sulphur, sulphur dioxide, is formed. This has a harmful action on vegetation, stone and metal-work, etc. In power stations, therefore, where coal is burned in very large quantities in a restricted area, it is desirable that the sulphur dioxide be removed from the flue gases before their emission into the air. This can be done by spraying the flue gases with a slurry or fine suspension of lime or chalk in water. The flue gases are then discharged into the air practically free from smoke, grit and sulphur dioxide.[1]

SOLID ILLUMINANTS

At the present time when, by the mere touch of the finger on a button, a flood of brilliant light can instantly be obtained, it is difficult to realize what must have been the conditions of life when man had to be content with the smoky flame of the pine torch or of the rush dipped in olive oil. When, also, one thinks of the old guttering candle, with its constant need of 'snuffing,' one can appreciate how great has been the advance in artificial illumination.

The production of light depends in all cases, with the exception of electric light, on the process of combustion in air, and it is therefore only what one would expect, that man first made use of those naturally occurring substances and materials which can be burned without requiring previous special treatment.

---

[1] Should it be found economically possible, the flue gases might be washed with ammoniacal liquor from gas-works and coke-oven plants. Thereby air pollution by sulphur dioxide would be avoided and valuable substances, ammonium sulphate and sulphur, could be obtained.

Thus the vegetable oils, such as olive oil and rape-seed oil, furnished, from a very early period, the main light-giving material; and at a later date, the need of a vessel to contain the oil was done away with by using solid animal fats in the form of candles.

In the earliest candles, the wick was made from the dried pith of the rush (hence the old name *rushlight*), but later, wicks of cotton fibre were employed, and the candle was formed by repeatedly dipping the wick into melted fat or tallow, and so men called them *dips*.

Early in the nineteenth century it was shown by the French chemist, CHEVREUL, that the solid animal fats are compounds of the familiar substance glycerine, $C_3H_5(OH)_3$, with various acids, more especially *stearic acid* ($C_{17}H_{35}{\cdot}COOH$). This acid, readily obtained by the decomposition of fat by superheated steam, displaced tallow as a candle-making material and it forms, generally with the addition of a small amount of solid paraffin (p. 55), the material of the more costly stearin candles of the present day. These burn with a bright and smokeless flame. The cheaper candles now in more widespread use are made of solid paraffin. They have a more translucent appearance than the stearin candles, and are not so hard.

Beeswax and other waxes have at various times and in various countries also found use in candlemaking.

When a candle is lit, the heat of the flame melts a small quantity of the solid candle material, and the liquid rises up the wick by what is known as capillary action—just as one can mop up water with a piece of blotting paper. The liquid is there vaporized, and it is the burning vapour that gives rise to the flame.

To obviate the necessity for 'snuffing,' or removing the unburnt end of the wick with a pair of special scissors, an operation so very necessary in the olden days, twisted or flat-plaited wicks are now used. As the candle burns the end of the wick curls or bends outwards to the edge of the flame and, coming in this way into contact with the oxygen of the air, burns away. This ensures that the wick does not grow too long and that the amount of liquid fuel conducted up into the flame is not more than can be properly consumed. The flame thus burns without smoke.

LIQUID FUELS AND ILLUMINANTS

The occurrence of a natural mineral oil has been known from a very early period, and 'slime' or bitumen (formed from mineral oil or petroleum,[1] by the loss of its more volatile constituents) was used as a mortar by the builders of the Tower of Babel. Classical writers, also, record the presence of oil in various regions and describe its use both as an embrocation and as an illuminant. In the region of Baku on the Caspian Sea, moreover, the 'Holy Fire' of the burning oil and of the gas which accompanies it was, in ancient times, a place of pilgrimage of the Persian Guebers or fire-worshippers.[2]

In America, exudations of mineral oil had long been known and the oil had, by reason of its medicinal and curative properties, been used both internally and externally. It was, however, only in 1859 that the first oil-well was drilled in Pennsylvania for the purpose of winning the oil for use as an illuminant and lubricant. The increasing demand for oil, for use more especially as a fuel, has, during the present century, led to the development and exploitation of many new oil-fields in different parts of the world.

Of the origin of petroleum, little can be asserted with confidence, but it is generally considered that the oil has been formed by the gradual decomposition, under bacterial action, of deposits of marine animal and vegetable matter. The oil occurs in pools between layers of impervious rock, and is associated with a gas, the pressure of which is, in some cases, sufficient to force the oil up through the bore-pipe so as to form a mighty fountain.

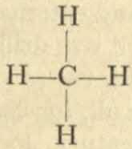
Although the petroleum from different oil-fields may vary greatly in composition, it consists, in all cases, essentially of a mixture of *hydrocarbons*, or compounds which contain carbon and hydrogen only. For the most part, the hydrocarbons belong to what is known as the methane or paraffin series (*see below*), but other hydrocarbons, known as *naphthenes*, may also be present in varying amounts. These compounds contain a lower proportion of hydrogen and are more akin to the so-called *aromatic* hydrocarbons (benzene, toluene, etc.),[1] which are also contained in coal-tar (*Chap.* 13). Small amounts of these aromatic hydrocarbons are also present in certain types of petroleum.

---

[1] The word petroleum means 'rock oil.'

[2] In the hills near Kirkuk in Iraq lies a shallow depression where inflammable gas, escaping from the crust of the earth, burns continuously, night and day, with dancing, flickering flames. This spot, known locally as the 'Fiery Furnace,' may have been the scene of the 'trial by fire' to which Shadrach, Meshach and Abednego were subjected by Nebuchadnezzar.

METHANE, or marsh gas, is the lowest member of a long series of hydrocarbons, all of which have similar chemical properties and composition. The molecule of methane consists of one atom of carbon to which four atoms of hydrogen are united; and since an atom of carbon is never found to combine with more than four atoms of hydrogen, the carbon is said to be saturated, and methane is spoken of as a *saturated hydrocarbon*. The molecule of methane can be represented diagrammatically thus:



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & H \\ & & | & & \\ & & H & & \end{array}$$

or, more simply, by the formula CH_4.

Methane is the inflammable gas which rises in bubbles when one stirs the mud of decaying vegetation at the bottom of a stagnant pool—hence the name *marsh gas*; and it is also the gas which, produced during the formation of coal,[2] escapes from the coal-beds during mining and which, mixed with the air of the mine, constitutes the explosive mixture, *fire-damp*. Methane, moreover, is the main constituent of the 'natural gas' which escapes from the earth in various oil-bearing regions (p. 59).

Large quantities of methane are produced by bacterial action on the sludge formed in the processes of sewage purification. In one installation, more than a million cubic feet of gas, containing 70 per cent. of methane, are produced daily. Since methane finds many important uses not only as a fuel but also in chemical industry, for the production of carbon black, hydrogen, methanol, etc., waste of it should be avoided and increased production and utilization should be encouraged.

---

[1] The name *aromatic* was given by chemists to these substances because it was found that the sweet-smelling compounds present in aromatic spices had a molecular structure closely related to that of benzene (*Chap.* 12).

[2] Many millions of cubic feet of methane are now piped off from the coal seams in British collieries alone. In this way a very valuable supply of fuel is obtained for the production of power at the collieries, and the mines are also rendered safer.

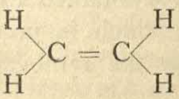
Carbon is remarkable among all the elements in the property that its atoms can combine with one another so as to form 'chains' of carbon atoms and give rise to a series of compounds which may be represented by the formulæ:

$$CH_3—CH_3 \text{ (ethane); } CH_3—CH_2—CH_3 \text{ (propane);}$$
$$CH_3—CH_2—CH_2—CH_3 \text{ (butane), etc.}$$

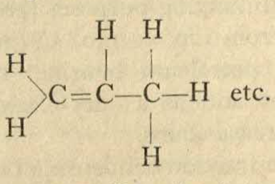
A large number of such compounds are known, and it will be observed that the composition of each of them can be represented by the formula C_nH_{2n+2}. They are *saturated hydrocarbons*. Owing to their chemical inertness, the hydrocarbons belonging to this series are spoken of as *paraffins*.[1]

As the proportion of carbon in the compounds increases, the hydrocarbons become less and less volatile, and boil, therefore, at higher and higher temperatures; and when the number of carbon atoms in the molecule is greater than sixteen, the compounds are solid at the ordinary temperature.

It may also be mentioned here that besides the saturated hydrocarbons, other hydrocarbons are known which contain a lower proportion of hydrogen, and are therefore said to be *unsaturated*. Thus, if two hydrogen atoms are removed from each of the compounds of the methane series, hydrocarbons are obtained which can be represented by the formulæ:



C_2H_4 (Ethylene)



C_3H_6 (Propylene)

These constitute another series of hydrocarbons, known by the name of the first member ethylene. Some of these hydrocarbons occur in the gas produced in the 'cracking' of oil (p. 55), and they are the raw materials for the production of 'polymer petrol' (p. 58) and for the manufacture of solvents and other substances of great value.

---

[1] From the Latin *parum* (little) and *affinitas* (affinity).

Hydrocarbons are also known which contain a still lower proportion of hydrogen, or higher proportion of carbon, for example acetylene, C_2H_2 or $HC{\equiv}CH$, the first member of a series having the general formula C_nH_{2n-2}.

Crude Petroleum is generally a thick yellow, brown, or black liquid, which shows a green fluorescence. After the gaseous hydrocarbons which may be dissolved in it have been removed, the petroleum has to be refined or purified and then submitted to *fractional distillation*, in order to separate it into portions adapted for different purposes.

The crude petroleum is heated in a still and the vapour led into a high tower fitted with perforated transverse plates, at which condensation of the vapour takes place. The constituents of higher boiling-point condense at the lower, hotter plates, and the vapour of the more volatile constituents bubbles through the liquid and condenses at successively higher levels. By tapping off the condensed liquid at different heights of the tower, a series of 'fractions' of different boiling-points can be obtained[1] (Plate 8.)

The most volatile fraction, which distils over up to a temperature of about 70° C. (158° F.), is called petroleum ether and is largely used as a solvent and as a local anæsthetic owing to the cold produced by its evaporation. The next fraction, with a distilling temperature between 70° and 120° C. (248° F.), is called gasoline or petrol, and is used as a motor spirit and also for illuminating purposes (petrol-air gas). At a higher temperature, from 120° to 150° C. (302° F.), there is obtained a fraction called petroleum benzine[2] or benzoline, which is used as a solvent and as a 'dry-cleaning' agent for the removal of oil and grease stains.

The fraction condensing between 150° and 300° C. (300° and 570° F.) constitutes kerosine,[3] burning oil, or paraffin oil; that condensing between 250° and 340° C. (482° and 644° F.) constitutes solar oil or gas oil, which is used in Diesel engines. The distillation of the less volatile residues is then carried out under reduced pressure and oils of various grades are obtained and are used as lubricating oils and for burning under boilers. From the highest fractions of all one obtains vaseline and, in some cases, solid paraffin, which is used for making candles, water-proofing paper, and other purposes. A final residue of pitch is obtained.

---

[1] The temperatures at which the different fractions are collected may vary in different refineries. The processes of refining also will vary in detail according to the nature of the crude petroleum.

[2] Not to be confused with benzene obtained from coal-tar.

[3] This spelling, with the termination -ine in place of -ene, has been adopted by international agreement.

Nearly all crude petroleum oils contain compounds of sulphur, and compounds of nitrogen are also frequently present in small amount. These pass over into the various 'fractions' obtained by distillation and have to be removed by suitable chemical treatment before the finished products are placed on the market.

In the refining process the sulphur compounds in the oil are converted into sulphuretted hydrogen, H_2S, from which, by controlled combustion, the valuable element, sulphur, can be recovered.

Since paraffin oil, or kerosine, contains a relatively large proportion of carbon, its vapour burns with a smoky flame, owing to incomplete combustion, unless there is a liberal supply of air. When this oil is used as an illuminant, therefore, the flame is surrounded by a chimney whereby a draught of air is created, and oxygen is thus brought in larger amount to the flame; and in the case of lamps with a circular wick, a tube must also be provided through which air can pass to the *inner* surface of the flame.

Until well into the present century, petroleum was of importance chiefly as a source of illuminants and lubricants, but its value now depends mainly on its being a source of fuel supply. Since 1 lb. of fuel oil, the higher boiling fractions of petroleum, has a calorific value of about 19,500 B.Th.U.—about one and a quarter times greater than anthracite—and since oil possesses many advantages over coal in the matter of cleanliness, control of consumption, stowage room, etc., its use as a fuel, especially for ocean steamers, has greatly increased.

It is, however, in the use of gasoline or petrol as a fuel for the internal combustion, motor-car and aeroplane engine that the greatest developments have taken place; and as the gasoline fraction obtained by the distillation of petroleum is quite insufficient to meet the demand, large quantities of motor spirit have to be produced by the 'cracking' of gas oil and even of kerosine, for which now there is a greatly reduced demand.

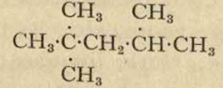
By heating these oils under pressure to a temperature of 380° C. (716° F.), or more, the relatively large molecules are broken down into the simpler molecules of the hydrocarbons which constitute gasoline or petrol. This process is facilitated by the presence of aluminium chloride which acts as a catalyst (*see Chap.* 7). The spirit obtained by 'catalytic cracking' ('cat. cracking') contains also unsaturated hydrocarbons (p. 53), as well as iso-paraffins[1] and so-called aromatic hydrocarbons (benzene, toluene, etc.). These are of value because they help to prevent the unpleasant phenomenon of 'knocking,' which is due to the passing of the relatively slow wave of combustion into the relatively very rapid wave of explosion in the gasoline-air mixture in the engine cylinder. Detonation or explosion takes place when the compression of the gasoline-air mixture exceeds a certain value for a given fuel.

Motor petrol is also produced by *platforming*, *i.e.* by cracking the lighter oils in the presence of platinum catalyst and hydrogen.

Since the efficiency of the internal combustion engine increases with the degree of compression of the fuel-air mixture in the cylinder before firing, it is of advantage to use a fuel which has little tendency to detonate on compression, or which has, as it is said, a high anti-knock (or high octane) value.[2] The tendency of a motor spirit to knock varies with the composition and nature of the hydrocarbons of which the spirit is made up, and great advances have been made in recent years in the production of motor fuels of high octane number by blending the gasoline obtained by the distillation of petroleum with 'cracked' spirit, benzene (benzole) or lead ethyl,[3] $Pb(C_2H_5)_4$, spoken of popularly

---

[1] In the iso-paraffins the carbon atoms are joined together so as to form not a *straight* but a *branched* chain, as is shown by the formula for iso-octane:



$$CH_3\cdot\underset{CH_3}{\overset{CH_3}{C}}\cdot CH_2\cdot\overset{CH_3}{CH}\cdot CH_3$$

[2] The anti-knock value of a motor spirit is determined by comparison with the anti-knock value of known mixtures by volume of the two hydrocarbons, normal heptane (C_7H_{16}) and iso-octane (C_8H_{18}) having the formula $(CH_3)_3\cdot C\cdot CH_2\cdot CH\cdot(CH_3)_2$. A motor fuel which has the same anti-knock properties as a mixture of 70 volumes of octane and 30 volumes of heptane is said to have an octane number of 70. 'Ethyl petrol' has an octane number of 80. The higher the octane number, the smaller is the tendency to knock.

[3] To prevent deposition of lead compounds on the sparking plugs, etc., ethylene bromide is added to the lead ethyl.

as 'Ethyl.' By blending petrol with up to 40 per cent. of isopropyl ether (produced from propylene), a motor fuel with an octane number of 100 can be obtained. Through the introduction of these improved motor fuels, the motor-car engineer has been able to design his engine so as to increase the compression ratio from about 4 : 1 to 7 : 1, or more. The efficiency has thereby been very greatly increased.

The natural reserves of oil are not inexhaustible, and the question arises whether any substitute can be obtained. Fortunately, the outlook is full of hope.

In Scotland, ever since 1860, mineral oil has been obtained by heating a carbonaceous shale, called *oil shale*. From one ton of this shale one can obtain about thirty gallons of oil from which, by distillation, motor spirit, illuminating oil, fuel oil, lubricating oil and solid paraffin can be obtained.[1] Since enormous deposits of oil shale occur in many different countries, it will be possible to obtain abundant supplies of oil fuel—at a greater cost it may be than at present—when the oil-wells shall have ceased to flow.

From coal, also, fuel oil may be obtained, and is being obtained, by various processes. By the low temperature carbonization of bituminous coal (p. 48) a tar is produced from which one can obtain, by fractional distillation, motor spirit, fuel and lubricating oils, similar to those obtained from petroleum; whereas by the high temperature distillation of coal (p. 61) a tar is produced from which benzene (or benzole)[2] is obtained. Although benzene is not used as a motor spirit by itself, mixtures of benzene with petrol and also with alcohol are extensively employed. The addition of benzene to petrol increases the anti-knock value.

Motor spirit can also be produced, and has been produced in very large amounts, by the hydrogenation of coal, a process developed originally by the German chemist, F. BERGIUS. Ground coal, made into a paste with oil for convenience of handling and treatment, is subjected to the action of hydrogen at a temperature of 420°–500° C. (say, 790°–930° F.), and under a pressure of about 200 atmospheres. The coal is thereby converted, by the action of heat and the taking up of hydrogen, into gaseous hydrocarbons (methane, ethane, propane, butane),[1] petrol, middle oils and heavy oil. The heavy oil is used for making the ground coal into a paste and the middle oils, in the form of vapour, are passed with hydrogen through heated tubes in the presence of molybdenum sulphide as catalyst. The oils are thereby 'cracked' and partially hydrogenated to saturated hydrocarbons, and the spirit so obtained is added to the petrol to produce a motor fuel with an octane number of 71–73. By the use of suitable catalysts, whereby the various reactions can not only be accelerated but also have their course directed, control is obtained of the nature of the oils formed. With tin as catalyst, in presence of hydrochloric acid gas, 180 gallons of motor spirit can be obtained by the hydrogenation of one ton of bituminous coal.

---

[1] Considerable quantities of ammonia are also produced, and the spent shale, consisting mainly of alumina and silica, is used for making building bricks.

[2] The term benzole is applied to various commercial mixtures of benzene hydrocarbons (benzene, toluene, etc.).

Petrol is also produced by the hydrogenation of coal-tar creosote (a process used in England) and of the tar produced in the low temperature carbonization of coal (p. 48). Moreover, increasingly large quantities of high-grade petrol are now also being produced from natural gas (p. 59) and from refinery gas, formed in the process of 'cracking' oils. These gases, which are available in enormous quantities, consist partly of saturated and partly of unsaturated hydrocarbons, The saturated hydrocarbons can be decomposed by heat, with formation of unsaturated hydrocarbons of the ethylene type. These unsaturated hydrocarbons, when passed at a temperature of about 450° F. and under a pressure of about 14 atmospheres over a catalyst, pyrophosphoric acid, undergo *polymeriaztion*, a process in which a number of simple molecules unite together to form more complex molecules. In this way motor spirit ('polymer petrol') of a high octane number, and even iso-octane itself, can be obtained, suitable for blending with and improving the antiknock properties of ordinary petrol.

In 1925, F. Fischer and H. Tropsch, in Germany, found that water-gas (p. 67), in presence of a suitable catalyst (*e.g.* cobalt and thorium) and at a temperature of about 400° F., is converted into a mixture of liquid and gaseous hydrocarbons. The low-boiling fraction of the liquid has a low anti-knock value and must be improved by the addition of lead ethyl, benzole, or the 'polymer petrol' just described; but the higher-boiling fraction, on being 'cracked,' gives good yields of high anti-knock motor spirit.

---

[1] The propane and butane are separated and compressed into cylinders for use as a gaseous fuel ('Calor Gas'), while the other gaseous hydrocarbons can be used for the production of hydrogen (p. 123).

From water-gas, also, high-grade, viscous lubricating oils can be produced, with the help of aluminium chloride as catalyst.

In various ways, therefore, research chemists have succeeded in producing motor fuel and lubricating oils from coal, directly or indirectly, and from natural and oil-refinery gases; and they have so greatly improved the products that a gallon of petrol will, to-day, do twice as much work as a gallon did some twenty years or so ago.

In addition to the mineral oils, alcohol or spirits of wine (*Chap.* 15) is also used to some extent as a fuel for motor-car engines. Natalite, for example, is a mixture of alcohol and ether and is produced as a motor fuel in Natal, South Africa; and mixtures of alcohol with benzene and with petrol are also used as motor fuels. Although the calorific value of alcohol is not so high as that of gasoline, higher compressions can be used without detonation, or 'knocking,' taking place, and the increase of efficiency of an internal combustion engine with compression is so great that it may compensate for the lower calorific value of the alcohol. The possibility of a great extension in the use of alcohol as a motor fuel in the future must not be overlooked.

Although petroleum is chiefly valuable as being a source of supply of fuels and lubricants, it has now also gained a position of major importance as a raw material for the production of compounds of great value (*see Chap.* 13).

GASEOUS FUELS AND ILLUMINANTS

In various countries (the United States, Russia, Rumania, Canada, and others) great reservoirs of 'natural gas' are found, unassociated with oil, and this gas, of which the main constituent is methane,[1] is used not only for illuminating purposes but also as a fuel for steel manufacture, for the melting of glass, and for other industrial purposes. Its use for the production of motor spirit has just been discussed. As a fuel, natural gas is of great importance on account of its high calorific value of over 1000 B.Th.U. per cubic foot. This is twice as great as the calorific value of the gas obtained by the high temperature distillation of coal. In the United States, many million cubic feet of gas are daily conveyed many hundreds of miles through pipes to industrial centres, and it is now also proposed, in America, to transport methane in the liquid state in insulated tanks. It may also become possible to transport liquid methane overseas from many of the world's oil-fields where, at present, thousands of millions of cubic feet of the gas are burned daily as a waste product. Millions of tons of coal could in this way be saved.

---

[1] Methane constitutes about 85 per cent. of natural gas, and ethane about 12 per cent. Small quantities of propane and other gases are also present.

Although natural gas has a very great value in the countries where it is found, the most important gases used at the present day for the production of heat and light are those which are obtained, by one process or another, from coal, and more especially the gas which is obtained by heating coal in closed vessels or 'retorts,' out of contact with the air. That a combustible gas can be produced in this way was observed, about 1688, by John Clayton, a Yorkshire clergyman, who later became Dean of Kildare; but it is to a Scotsman, William Murdoch, that belongs the credit of having developed the process for the production of an illuminating gas for general use.[1] That was towards the end of the eighteenth century, but it was only after the lapse of ten or twelve years that the gas began to be publicly and generally used. The introduction of gas for street lighting was due to a Moravian, Winzer or Winsor, and through his efforts Pall Mall in London was lit by gas on 28th January 1807, and created quite a sensation (Plate 7). By 1816 the greater part of London was lit by gas. The great change which was thereby effected in the appearance of the town and in the comfort of the people is described by a writer in the early nineteenth century: 'We all remember the dismal appearance of our most public streets previous to the year 1810; before that time, the light afforded by the street lamps hardly enabled the passenger to distinguish a watchman from a thief, or the pavement from the gutter. The case is now different, for the gas-lamps afford a light little inferior to daylight and the streets are consequently divested of many terrors and disagreeables, formerly borne with because they were inevitable.'

---

[1] William Murdoch (or Murdock), who was born at Lugar in Ayrshire, in 1754, was associated with the engineering firm of Messrs. Boulton & Watt, Birmingham. In 1792 he lighted his house at Redruth, in Cornwall, with coal-gas, and it was at the works of Boulton & Watt at Soho, Birmingham, that coal-gas was first used (in 1798) on a large scale as an illuminant.

Coal is not a definite chemical substance, but a complex mixture of substances, the nature of which is not yet definitely known. The essential elementary constituents of coal are carbon, hydrogen and oxygen, but the elements nitrogen and sulphur also occur in small amounts; and when coal is heated in closed retorts, or carbonized as one says, there is obtained not only the gas which is used for illuminating and heating purposes, but also considerable quantities of ammonia and of tar, and there remains in the retort a residue of coke. Down to the middle of last century the ammonia and the tar were regarded as by-products of little value, but, as we shall learn more fully later, they have since then become materials of great importance; while, owing to the great development of the iron and steel industry, the demand for coke has, in recent times, become so great that many millions of tons of coal are now carbonized annually for the production, primarily, not of gas, but of coke.

Although the nature of the products and their relative amounts depend on the kind of coal carbonized and on the temperature at which the process is carried out, one may say that, under the general conditions met with in gas-works, the main products obtained and their relative amounts are as follows:

	Approximate quantity formed from 1 *ton of coal*
1. Illuminating gas	11,000 cubic feet.
2. Coal-tar	120 lbs.
3. Ammonium sulphate	25 ,,
4. Coke	1,500 ,,

In the manufacture of coal-gas, the coal is heated in large fire-clay retorts, placed horizontally or vertically, at a temperature of 1000°–1100° C. (say, 1800°–2000° F.), and the products of decomposition are led away by a pipe the mouth of which dips under the surface of water contained in what is known as the hydraulic main (Fig. 8). Here, part of the water and of the coal-tar condenses, while the gaseous products pass away to a series

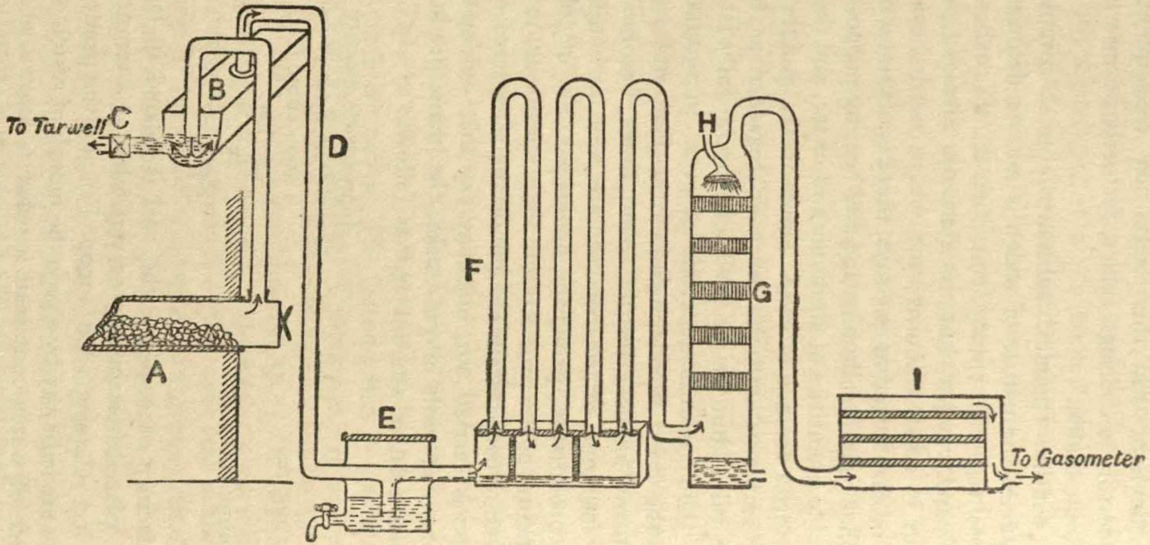


FIG. 8.—DIAGRAM OF GAS-MANUFACTURING PLANT

A, retort in which coal is heated; B, the hydraulic main; C, outlet for the tar; D, gas pipe; E, tank in which the ammoniacal liquor collects; F, cooling pipes; G, scrubber in which traces of ammonia are removed by trickling water, supplied through the sprinkler H; I, purifying boxes for removing carbon dioxide and sulphuretted hydrogen.

of cooling pipes, exposed to the air, in which a further condensation of water vapour and of tar takes place. The ammonia present in the gas dissolves for the most part in the water produced, and the remainder is removed by passing the gas through 'scrubbers.' The gas still contains a number of substances the presence of which would be deleterious, the more important of these being carbon dioxide and sulphuretted hydrogen (hydrogen sulphide, H_2S). This latter gas it is which, formed by bacterial action on sulphur compounds, has the smell of rotten eggs, gives to the picturesque canals of Venice the atmosphere of an open sewer, and imparts their special virtue to the waters of Aix-les-Bains and Harrogate. It is also the gas which causes the tarnishing of silver.

Sulphuretted hydrogen is harmful in coal gas because it gives rise, in the burning gas, to sulphur dioxide (the pungent gas formed when sulphur burns in air), which exercises a destructive action on plants, metal-work, etc.; and the presence of carbon dioxide is objectionable because it lowers the heating and illuminating power of the gas. The gas is freed from these impurities by passing it, first of all, through a series of boxes containing trays covered with slaked lime which combines with and so removes the carbon dioxide; and then through another series of boxes containing hydrated oxide of iron (*e.g.* bog iron ore), which removes the sulphuretted hydrogen, by forming with it the compound, sulphide of iron. By introducing a small and regulated amount of oxygen into the gas at this stage, the sulphide of iron is continuously oxidized to iron oxide and free sulphur. When the amount of free sulphur reaches about 60 per cent. of the iron oxide, the latter loses its efficacy, but this 'spent oxide' still has its uses, for it is sold to the manufacturer of sulphuric acid, who utilizes it in the manner we shall learn later.

Besides hydrogen sulphide, other substances—carbon disulphide, naphthalene and hydrocyanic acid (prussic acid)—are also removed from coal-gas and form or give rise to by-products of value. Among the by-products obtained is ammonium thiocyanate, NH_4CNS, which, on being heated, forms the compound *thiourea*, $CS(NH_2)_2$. This compound is used in the production of synthetic plastics; and it is the essential consituent in certain silver-cleaning liquids.

After undergoing the various processes of purification, the gas passes to the gas-holder, and is then ready for distribution to the consumers. Although the composition of the gas supplied by different works is by no means the same, nor invariable even in the case of the same works, the following numbers may be taken as representing an average composition of illuminating gas.

COMPOSITION OF COAL-GAS

Hydrogen	56	per cent. by volume.
Methane	22·8	,, ,,
Unsaturated hydrocarbons (Ethylene, etc.)	2·5	,, ,,
Carbon monoxide	10·9	,, ,,
Carbon dioxide	1·3	,, ,,
Nitrogen	6·0	,, ,,
Oxygen	0·5	,, ,,

Coal-gas, then, as we see, is a mixture of a number of gases, and of these carbon dioxide, nitrogen and oxygen represent what we may call impurities; they act merely as diluents and lower the illuminating power of the gas.

Of the combustible gases present in coal-gas, hydrogen burns with a non-luminous, scarcely visible flame; carbon monoxide, with a non-luminous flame of a bright blue colour;[1] methane, with a slightly luminous, and ethylene, with a strongly luminous flame. It is, no doubt, to the decomposition of hydrocarbons, especially unsaturated hydrocarbons, with liberation of finely divided particles of carbon, that the luminosity of a coal-gas or candle flame is due, the carbon particles being raised to incandescence by the heat of the flame. When the particles reach the edge of the flame and come in contact with the oxygen of the air, they are completely burned to the invisible gas, carbon dioxide.

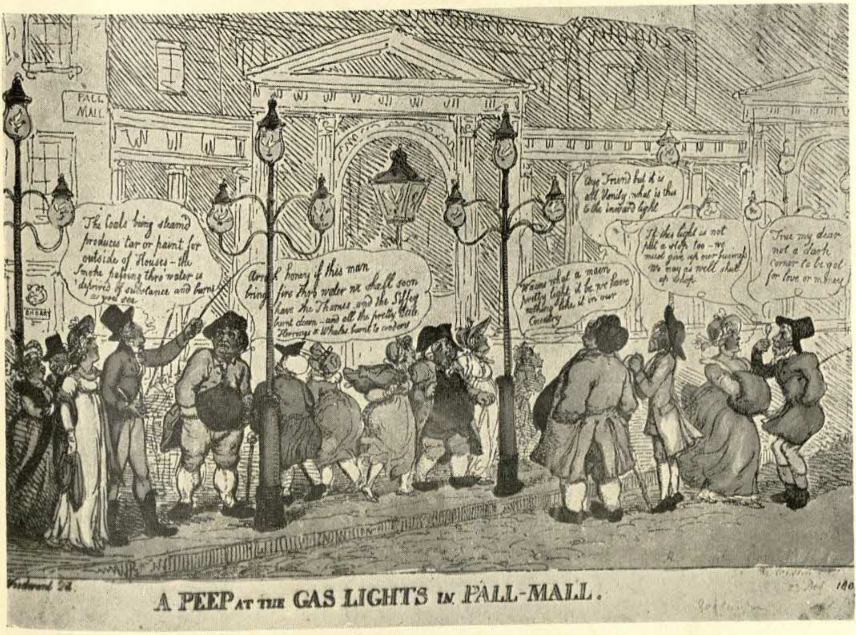
The luminosity of a flame, it will now be understood, can be increased by introducing carbon-yielding substances, *e.g.* unsaturated hydrocarbons, into the burning gas. It is thus possible to 'enrich' a poorly luminous gas.

Coal gas is now used mainly as a domestic and industrial fuel for the production of heat, and the consumer pays for the amount of heat energy, or the number of *therms*, he receives, 1 therm being equal to 100,000 B.Th.U.

---

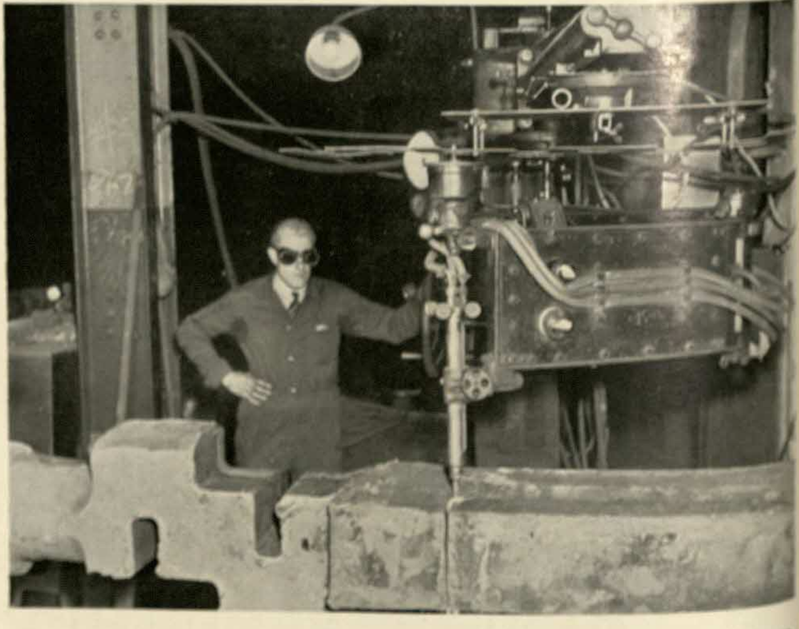
[1] The lambent blue flame seen on the top of a clear-burning coal fire is due to the combustion of carbon monoxide.

6. ANTOINE LAURENT LAVOISIER


PALL MALL
The Coals being steamd produces tar or paint for outside of Houses – the Smoke passing thro' water is deprived of substance and burns as you see
Arrah honey if this man brings fire thro water we shall soon have the Thames and the Liffey burnt down – and all the pretty little Herrings & Whales burnt to cinders
Waune what a mein pretty light it be we have nothing like it in our Country
Aye Friend but it is all Vanity what is this to the inward light
If this light is not put a stop too – we must give up our business We may as well shut up shop
True my dear not a dark Corner to be got for love or money
Woodward Del.
A PEEP AT THE GAS LIGHTS IN PALL-MALL.

7. A PEEP AT THE GASLIGHTS IN PALL MALL
After a drawing by Woodward. Engraved by Rowlandson

8. A MODERN PETROLEUM DISTILLATION UNIT



9. CUTTING A STEEL SHAFT BY AN OXY-ACETYLENE FLAME

When coal-gas is used as a fuel for heating purposes, it is important that combustion takes place rapidly and completely without the separation of carbon particles, and this result is secured if the coal-gas, before being burned, is mixed with a suitable amount of air. The molecules of the combustible gas then find oxygen with which they can combine, ready at hand, so to say, and combustion takes place rapidly and completely without the separation of carbon particles; the flame is therefore non-luminous, but much hotter than the ordinary luminous flame. This principle was made use of by the German chemist Bunsen in the burner which goes by his name, and is applied in gas fires, gas cookers, etc. (Figs. 9 and 10). In the Bunsen burner, the gas issues from a jet surrounded by a wider tube, near the foot of which holes are pierced. Through these, air is drawn into the burner by the uprush of gas. The gas thereby becomes mixed with air, the amount of which necessary to ensure complete combustion can be regulated by enlarging or diminishing the size of the air openings. If too much air is admitted to the gas, the mixture becomes explosive, and the flame strikes back to the jet where the gas enters the burner. If this occurs, the gas must be at once turned off, as incomplete combustion takes place and products of a very poisonous character are formed. These, fortunately, betray their presence by a powerful and unpleasant odour.

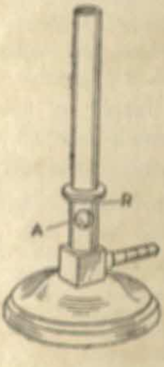


Fig. 9.—Bunsen Burner

A, air-hole by which air can pass into the tube and mix with the gas which enters at the small jet seen through the opening. The supply of air can be regulated by means of the movable ring R.

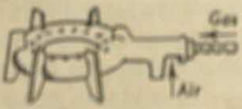


Fig. 10.—Gas Cooker, constructed on the principle of the Bunsen Burner

In gas fires, burners of the same type as the Bunsen burner are employed, and the long, hot gas flames which are formed raise to a high temperature special 'radiants' of fire-clay and asbestos, which then radiate heat into the room.

If the luminous coal-gas flame is supplied with oxygen instead of with air, a higher temperature can be obtained; for the nitrogen of the air acts as a diluent and so cools down the flame. One cannot, however, in this case make use of the ordinary burner, for the mixture of oxygen and coal-gas is explosive, and the flame would at once 'strike back.' A burner of special construction is therefore employed which allows a jet of oxygen to be blown into the gas as it burns at the mouth of the burner, and one thus obtains what is known as the oxy-coal-gas blowpipe flame (Fig. 11).

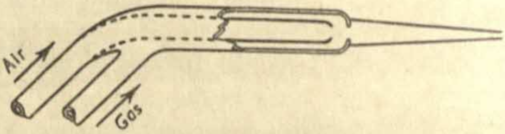


FIG. 11.—BLOWPIPE
When the gas is burning at the mouth of the wider tube, air or oxygen is blown into the flame through the inner tube.

The carbonization of coal for the production of town-gas requires for its success a particular kind, or particular kinds, of coal, supplies of which, unfortunately, are becoming more difficult to obtain. Moreover, only about 25 per cent. of the heat units in the coal are obtained in the gas, and about 50 per cent. are retained in the residual coke. Processes, however, have been worked out for the complete gasification of coal, especially of coal not altogether suitable for the production of gas by carbonization. By passing steam, under a pressure of 20–30 atmospheres, through a bed of coal maintained at a sufficiently high temperature by the addition of oxygen to the steam, the coal can be converted into gas without solid residue (Lurgi process). By suitably controlling the process, a mixture consisting essentially of hydrogen, carbon monoxide and methane (*e.g.* hydrogen 62, carbon monoxide 22, methane 14, carbon dioxide 2 per cent.) can be obtained. This has a high calorific value and can be used as a fuel in place of ordinary coal-gas.

OTHER GASEOUS FUELS

Not only can a gaseous fuel, coal-gas, be obtained by the carbonization of coal, but an important industrial gaseous fuel is also produced, in large amount, by passing steam through white-hot coke. A mixture of carbon monoxide and hydrogen is thereby obtained. Thus:

$$C + H_2O = CO + H_2$$

Carbon (coke) and water give carbon monoxide and hydrogen.

Although this gas mixture, known as *water-gas*, has no illuminating power, it can be manufactured at a relatively small cost, and after being enriched by the addition of unsaturated hydrocarbons, obtained by the decomposition or 'cracking' of oil at a high temperature, it is added (as *carburetted water-gas*) to the gas obtained by the carbonization of coal. Water-gas is also frequently added without enrichment to coal-gas, so as to give a cheaper gas of lower calorific value.

Coal-gas, produced by high temperature carbonization, has a calorific value of about 480–520 B.Th.U. per cubic foot; while that produced by low temperature carbonization has a value of 800–1000 B.Th.U. per cubic foot. The calorific value of water-gas, which is largely used as an industrial fuel, alone or mixed with coal-gas, is about 280 B.Th.U. per cubic foot.

Another gaseous fuel, *producer gas*, a mixture of carbon monoxide and nitrogen, is produced by passing air through incandescent coke; and by passing a mixture of steam and air through red-hot coke a mixture of carbon monoxide, hydrogen and nitrogen, known as *semi-water-gas*, is obtained. This is a convenient source of nitrogen and hydrogen for the industrial production of ammonia (p. 131).

HYDROGEN finds a number of very important uses in industry, *e.g.* synthesis of ammonia, hydrogenation of coal, hydrogenation of oils. When hydrogen burns in air or in oxygen, water, H_2O, is formed with production of a large amount of heat.[1] This fact is made use of in the oxy-hydrogen blowpipe flame, by means of which a temperature of about 2000° C. (say, 3630° F.) can be obtained. The high temperature thus produced has found an interesting and important application in the manufacture of artificial gems, such as rubies and sapphires. These gems consist essentially of oxide of aluminium (alumina), a substance which occurs naturally as corundum, and, in an impure state, as emery. It is a very refractory substance, but it can be melted in the oxy-hydrogen blowpipe flame. When a mixture of 97·5 per cent. of alumina and 2·5 per cent. of oxide of chromium is heated in the blowpipe flame, it is fused, and, on cooling, solidifies to a ruby-red solid, which is in fact, ruby, identical in physical and chemical properties with the natural gem. It differs from the latter solely in minute irregularities of internal structure detectable only by the eye of the expert. These artificial rubies, on account of their great hardness, are now manufactured in large quantities for use in the bearings of watches and for other purposes.

---

[1] A mixture of hydrogen and oxygen explodes with great violence when ignited.

Sapphires can be obtained by fusing a mixture consisting of alumina and small quantities of the oxides of titanium and iron.

In a similar manner, single crystals of *rutile* (titanium oxide), of a very pale straw colour or coloured by the addition of small amounts of metal oxides, are produced as gem stones. Owing to their very high refractive power, they rival the diamond in brilliance.

A temperature higher than that of the ordinary oxy-hydrogen blowpipe flame can be obtained with the *atomic hydrogen flame*. When hydrogen is passed through an electric arc between tungsten electrodes, the molecules are dissociated into atoms; and as these atoms pass beyond the arc they recombine to form molecules. In this process a large amount of heat is liberated, and this is added to the heat of combustion. A temperature of about 3500° C. can thereby be obtained.

Besides water, hydrogen can form with oxygen the compound *hydrogen peroxide*, H_2O_2, which is now produced industrially in large amount. The compound readily yields up oxygen and finds use as an oxidizing and bleaching agent and as an antiseptic. It is used in cleaning paintings and as an aerating agent in the production of foam rubber; and it is also a valuable chemical reagent. The decomposition of hydrogen peroxide into water and oxygen is greatly accelerated by platinum, and the oxygen so formed is mixed with the vapour of petrol or other oil to increase the temperature of combustion in certain rocket and power units.

CARBON MONOXIDE differs from the other oxide of carbon,

carbon dioxide, to which reference has already been made, not only in being a combustible gas but also in being intensely poisonous. This is due to the fact that the gas combines with the hæmoglobin, or oxygen-carrying constituent of the blood, to form a very stable, bright-red compound, carboxy-hæmoglobin, which is no longer able to take up oxygen from the air entering the lungs. The presence of 1 volume of carbon monoxide in 5000–10,000 volumes of air will cause headache, while if 1 per cent. of carbon monoxide is present, unconsciousness and death will occur in a few minutes. Many cases of poisoning by carbon monoxide have occurred owing to its presence in town gas and in the products of imperfect combustion in stoves or in the engines of motor cars, from which it passes out in the exhaust. In cases of necessity, protection against the gas can be obtained by wearing a mask containing a mixture of the oxides of manganese, copper, cobalt and silver—a mixture known technically as *hopcalite*. In the presence of this mixture, or even of a specially prepared manganese dioxide alone, carbon monoxide is oxidized by atmospheric oxygen to carbon dioxide.

When carbon monoxide is passed, along with chlorine, over activated charcoal, which acts as a catalyst, a gaseous compound, carbonyl chloride, $COCl_2$, or *phosgene*, is formed. It finds very important applications in the industrial production of dyes and other substances.

ACETYLENE, a gas which for a number of years was widely used as an illuminant, now finds use mainly as a fuel and as an important raw material in chemical industry. It is produced by the action of water on calcium carbide, a substance obtained by heating to a high temperature a mixture of quicklime (calcium oxide) and carbon in the form of anthracite or coke. The preparation is carried out in a special type of furnace in which the high temperature necessary is obtained by means of the electric arc,[1] and owing to its use for the production of acetylene, calcium cyanamide (*Chap.* 8), and other substances, calcium carbide is now manufactured in large quantities.

Acetylene is also produced by the thermal decomposition (pyrolysis) of methane and higher hydrocarbons.

Acetylene is an unsaturated hydrocarbon, having a relatively large proportion (over 92 per cent.) of carbon, as is shown by its formula C_2H_2. Under ordinary conditions the gas burns with a luminous and very smoky flame, but by using a special burner which ensures the admixture with the gas of a small amount of air, a white, intensely luminous flame is obtained.

---

[1] A temperature estimated at about 3000°C. (about 5400°F.) can, in this way, be obtained.

By injecting oxygen into a flame of acetylene, a temperature of about 3480° C. (6300° F.) can be obtained, and this fact has received important applications. If, for example, the oxy-acetylene flame is allowed to impinge on a piece of iron or steel, the metal is heated locally to redness, and if a fine jet of oxygen is then directed against the red-hot metal, the iron is oxidized to oxide of iron which melts in the intensely hot blowpipe flame, and flows away like water. By this means one can cut through even large steel rods, shafts, or girders as easily as a knife will cut through cheese, and with a cut almost as fine (Plate 9). One of the first applications to be made of the oxy-acetylene blowpipe flame was to cut through the dense tangle of iron girders formed by the collapse of the buildings in the fire at the Brussels Exhibition of 1910, and so to allow of their removal. Acetylene is also very extensively used for the welding of metals.

Owing to the readiness with which compressed or liquid acetylene may undergo explosive decomposition, the gas is generally dissolved in a solvent, *acetone*, under pressure, and the solution stored and transported in steel cylinders. These cylinders contain a porous, absorbent material which acts as a carrier for the solvent, acetone, and increases the storage capacity of the cylinder. The danger of explosion is also thereby diminished.

Besides being used in the manner described above, large quantities, about half the total production, of acetylene are used in chemical industry for the production of acetic acid (*Chap.* 15), ethyl alcohol, butyl alcohol, synthetic rubber, etc. Acetylene, in a concentration of about 1 per cent., is also used to accelerate the ripening of peaches, oranges and other fruits.

The carbonization of coal was first carried out for the production of an illuminating gas for general use; and throughout the greater part of the nineteenth century it was the main source of artificial illumination. With the introduction of electricity, however, its dominant position began to be vigorously assailed, and it is solely due to the invention of the now familiar incandescent mantle that coal-gas continues to be widely used for lighting even at the present day.

The 'mantles,' formed of woven cotton, rayon, or ramie fibre (produced from a plant of the nettle class), are soaked in a solution containing the nitrates of thorium and cerium[1] in the proper proportions. These mantles are then dried and incinerated, whereby the fibre is burned away and the nitrates are converted into a mixture of the oxides of the metals, which form a skeleton-work preserving the shape of the mantle. To protect the fragile mantle from injury during transport, it is dipped in collodion. When the mantle is suspended in the hot, non-luminous flame of a special burner constructed on the principle of the Bunsen burner, it is raised to incandescence and emits a brilliant white light. From a careful investigation it was found that the best results are obtained when the oxides are present in the proportion of 99 per cent. of thoria (thorium oxide) to 1 per cent. of ceria (cerium oxide).

---

[1] The chief source of these elements is a mineral known as monazite, which is found in various parts of the world, but more especially in Brazil and in Travancore, India.

Chapter 5

MATTER, ENERGY AND EXPLOSIVES

THE consideration of the process of combustion, controlled and utilized for the production of heat and light, leads to a realization of the fact that in the chemical reactions and transformations which take place, one is not dealing merely with material things. In the case of the burning candle, oil, or coal-gas, it is not the combustible substances (stearin, paraffin, hydrogen, methane, etc.), nor the products of combustion (carbon dioxide and water vapour), which interest us primarily, but the immaterial light to which the process of combustion gives rise. So also, passing on to the consideration of combustible substances as fuels, and of the process of combustion as a source of heat, we again recognize that our interest is focused not on the material nature of the combustibles, but on their efficiency as heat-producers. Heat, however, is a form of energy, and can be converted into other forms of energy, such as mechanical energy, and can perform what we call work; and so it is really in their power of doing work that we see the value of combustibles. The combustible substances together with the oxygen of the air represent so much *potential energy*, and the process of combustion is like the downward rush of the waterfall in being a process by which potential energy becomes available for doing work. In the recognition of the supreme importance of energy, in the establishment of the law of the conservation of energy and of the laws governing the mutual transformation of the different forms of energy, we see one of the greatest achievements of nineteenth-century physical science; and if one would grasp the spirit of modern chemistry, one must learn to regard a chemical change or reaction not merely as involving some material transformation but as representing a flow of energy out of or into the substances undergoing the change. 'Real gain,' as Sir William Ramsay said in his presidential address to the British Association in 1911, 'real gain, real progress consists in learning how better to employ energy—how better to effect its transformation'; and it is by the utilization of energy and by the methods of applying and transforming energy, that the nineteenth and twentieth centuries are so strongly marked off from the centuries which preceded them.

At the present day by far the greatest part of the energy necessary for the continuance of vital activity, as well as for carrying on the industrial life of the world, is derived from the energy of combustion of carbon and of its compounds. Through the oxidation (combustion) of carbonaceous food by means of the oxygen taken in through the lungs, the vital activity of the animal organism is maintained, and the inert carbon dioxide produced in the process is sent into the atmosphere in the expired air. But the carbon does not thereby cease to be available, for, as has already been pointed out (p. 24), green plants, absorbing the radiant energy of sunlight, transform and utilize the carbon dioxide for the purpose of building up their own structures and producing compounds like starch and sugar, which again become the food and the source of energy of animals. In the case, therefore, of the element carbon, which constitutes the basic element of all living matter, there is a continual circulation in nature, whereby the mutual preservation of the animal and vegetable worlds is secured. The green plants act as transformers of the radiant energy of sunlight into the potential energy of combustible substances.

It has been pointed out (p. 12) that the atoms of many elements do not exist as free atoms but combine to form molecules. This also is a chemical reaction which is associated with evolution of heat. Thus, when atoms of hydrogen combine to form molecules, a large amount of heat is evolved, a fact which is made use of in the atómic hydrogen blowpipe (p. 68).

Although the association of energy with chemical change is very obvious in the process of combustion, it is also found in all chemical changes. Every chemical system, every collection of substances which can spontaneously undergo chemical change, represents a certain amount of potential energy, and the material change which is observed, and which constitutes what is called a *chemical reaction*, is merely the outward sign of the conversion of so much potential energy into active energy—heat energy, or some other form of energy. Moreover, whenever a chemical change or reaction occurs, the heat which is given out, the so-called *heat of reaction*, is, for a given weight of the reacting materials and under specified conditions, constant and definite in amount.

It must not be thought, however, that all chemical change is accompanied by an *evolution* of heat. In some cases, the initial substances possess less energy than the final products, and the chemical change therefore takes place with *absorption* of heat. Energy, that is to say, must be supplied to the initial substances in order that they may pass into the final products of change. One distinguishes, therefore, between *exothermal* reactions or reactions accompanied by evolution of heat, and *endothermal* reactions or reactions accompanied by absorption or taking in of heat energy.

This way of regarding chemical change as being the outward and visible sign of energy change is very instructive; for it is clear that if we can make a substance take up energy—if we can, as it were, pump energy into a substance—we can thereby alter the amount of energy of which that substance is the carrier, and so change its nature. This fact is clearly illustrated by the behaviour of the familiar substance, oxygen.

The molecule of oxygen consists of two atoms, O_2, but when the gas is subjected to the action of an electric discharge under particular conditions, it takes up or absorbs some of the energy of the discharge and passes into a gas which, on account of its powerful and characteristic smell, received the name of *ozone* (Greek *ozo*, I smell). The material change, the chemical change, which accompanies the absorption of energy, is the addition of a third atom of oxygen to the molecule of that gas, so that the molecule of ozone consists of three atoms of oxygen, O_3. Since ozone contains more energy than ordinary oxygen, it is a more active oxidizing agent, and for this reason it is used for the purification of water and other bactericidal purposes, and for bleaching wax, starch, flour, ivory and other substances.

At Niagara Falls, large quantities of ozone are used in the production of vanillin, the sweet-smelling constituent of vanilla pods, by the oxidation of oil of cloves.

In white phosphorus and red phosphorus (p. 44), and in the three forms of carbon—charcoal, graphite and diamond—we have further examples of elements existing in different, so-called *allotropic*, forms containing different amounts of energy. That the three forms of carbon, which differ so markedly in appearance and physical properties, are associated with different amounts of energy, is shown by the fact that when equal weights are burned different amounts of heat are evolved. The applications and uses of the different forms of carbon, however, do not centre round their calorific values, but round other properties of quite a different character.

Diamond is a crystalline form of carbon which is now found mainly in South Africa, the Congo and Gold Coast, and is greatly valued as a gem. The crystals, generally in the form of octahedra, may occur either embedded in a rocky matrix, known in South Africa as blueground (Plate 10), from which they are recovered by crushing and washing, or in loose alluvial deposits. Diamond has a high index of refraction and, consequently, when suitably cut, scintillates and flashes in varied colours. It is the hardest of all substances and therefore finds important use as a cutting, drilling and polishing material. For this purpose the impure black diamonds, known as *carbonado* and as *bort*, are largely employed.

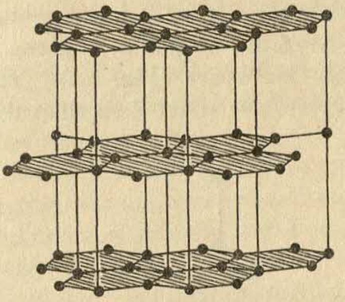


FIG. 12.—ARRANGEMENT OF THE CARBON ATOMS IN GRAPHITE

Graphite is also a crystalline form of carbon, deposits of which are found especially in Ceylon and Madagascar. It has a greasy or unctuous feel and is extensively used as a lubricant. Unlike diamond, graphite is soft and has long been used for the manufacture of lead pencils. For this purpose, the graphite is ground to a fine powder and mixed with various amounts of clay or powdered retort carbon in order to produce pencils of different hardness. On account of its resistance to heat, graphite is used for making crucibles. It is also a moderately good conductor of electricity and is employed in the construction of dry cells and of electrodes for use in electro-chemical industry (*Chap.* 10). Graphite is now mánufactured in large amount from anthracite and coke.

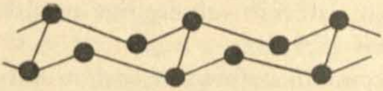


FIG. 13.—LAYER OF CARBON ATOMS IN DIAMOND

The marked differences in the properties of diamond and graphite are due to differences of crystalline structure, or arrangement of the carbon atoms in the crystal. In graphite, as is shown by examination with X-rays, the crystal consists of layers of carbon atoms, the atoms in each layer being arranged in the form of hexagons lying in one plane; and the different parallel layers are relatively far apart (Fig. 12). The forces acting between adjacent layers are much less than those between the atoms of the same layer, and the different layers can therefore move past one another relatively easily. This explains the soft, unctuous feel of graphite and its use as a lubricant.

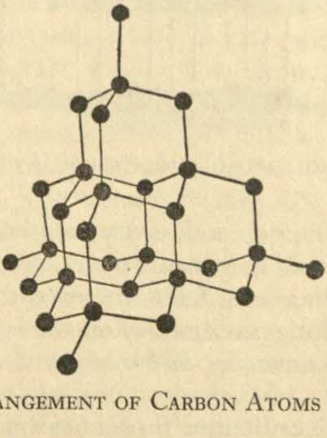


FIG. 14.—ARRANGEMENT OF CARBON ATOMS IN DIAMOND

In diamond there are also layers of carbon atoms arranged in hexagons. The atoms in a given layer, however, are not all in one plane, but have a zig-zag arrangement, so that the layers have, as it were, a corrugated surface (Fig. 13). The atoms in adjacent layers, moreover, are as near together as the atoms in a given layer (Fig. 14). The crystal is therefore more compact than graphite, and the adjacent layers, being near together and 'corrugated,' do not readily move past one another. Hence the hardness of diamond.

Charcoal was, from a very early time, used as a fuel and for the smelting of iron ores, etc., and in all the forests of Europe the 'coallier' or charcoal-burner was a well-known and picturesque figure. It may be that he still survives in some places and that a certain amount of charcoal is produced by the primitive, centuries-old and very wasteful method of the 'pit' in which lengths of wood were built up round a central chimney and set on fire. The combustion of part of the wood served to carbonize the rest. Now, however, charcoal is mainly obtained by heating wood, bone, coconut shell and other carbonaceous matter in a closed retort, out of contact with the air. Moreover, at the present day large quantities of wood are 'distilled' or carbonized not only for the production of charcoal but also for the sake of the other products formed.

When wood is heated in retorts, volatile products[1]—wood-tar, wood-spirit or methyl alcohol, acetic acid, acetone and various gases—pass off and charcoal remains in the retort. The gases are used for heating the retorts.

The 'pyroligneous acid' or aqueous distillate from wood was, until 1925, the main source of methyl alcohol (or methanol as it is now frequently called), acetic acid and acetone. These substances, however, all of which are important substances in industry, are now mainly produced by other processes which will be discussed in due course.

Charcoal is very porous and possesses in a very high degree the property of condensing on its surface, or *adsorbing*, different gases and vapours. This property can be greatly enhanced by a process of *activation*. The charcoal is heated first in a rapid current of air, in order to burn away hydrogen and hydrocarbons, and then in a current of steam at about 900° C. This active, or activated, charcoal or carbon is used for removing foul or noxious gases from the air, and finds important application in the construction of gas-masks for protection against poisonous gases. It is also used for removing gasoline vapour from 'natural gas' which escapes from many oil-wells, and for the recovery of benzene, carbon tetrachloride, acetone and other volatile liquids employed in dry-cleaning and other processes.

---

[1] Crude wood-spirit, which contains a number of substances besides methyl alcohol, is extensively used in Great Britain for the purpose of denaturing spirits of wine (ethyl alcohol).

The adsorptive power of charcoal is greatly increased by lowering the temperature and this fact is made use of for the purpose of producing high vacua. The vessel to be exhausted is connected with a tube containing charcoal cooled in liquid air. At this low temperature, the air in the vessel is very completely condensed on the surface of the charcoal.

Charcoal also finds a very wide use for the decolorizing of liquids, *e.g.* sugar molasses.

Carbon black, *lampblack*, or soot, another form of amorphous carbon, is produced by the combustion, in a limited supply of air, of coal-tar residues and also by burning natural gas and methane against a cold surface. It is used in the manufacture of printer's ink, Chinese ink, and boot-blacking. It is most extensively employed, however, in the manufacture of rubber tyres, because when mixed with the rubber it gives increased toughness, elasticity and durability. By this means, a fourfold increase in the mileage of a motor-car tyre can be obtained.

EXPLOSIVES

The idea that a spontaneously occurring change represents the conversion of so much potential energy into other forms of energy, can perhaps be most vividly realized from a consideration of the materials known as *explosives*. In the case of most of the explosives actually in use, the chemical process which occurs is essentially one of very rapid combustion, with production of gaseous substances occupying a volume which, at the temperature of the explosion, is, perhaps, 15,000 to 20,000 times as great as that of the explosive itself.

As early as the seventh century, we read, a rapidly burning mixture, known as Greek Fire, was used by the inhabitants of Constantinople in their defence of the city against the Moslems, and, even as late as the thirteenth century, rapidly burning mixtures of sulphur, pitch, naphtha and other substances which 'came flying through the air like a winged long-tailed dragon, about the thickness of a hogshead, with the report of thunder and the velocity of lightning,' were used by the Moslems in the crusades. When and by whom the first real explosive, *gunpowder*, was invented is unknown, although the invention has frequently, but erroneously, been attributed to Roger Bacon in the thirteenth century. During the nineteenth century, more especially, man strove to discover new explosives of greater and greater power, to learn how better to utilize and control the transformation of the great stores of potential energy contained in explosives, and to make them work for him both in peace and in war. Some idea of the advance which has been made is gained when we compare the artillery used by the English at the battle of Crécy in 1346, when the guns 'threw little balls of iron to frighten the horses,' with the modern large gun which can hurl a projectile of nearly a ton in weight to a distance of thirty miles.

Gunpowder is a mixture of potassium nitrate or saltpetre (KNO_3), charcoal and sulphur, and its action as an explosive depends on the rapid combustion of the sulphur and charcoal at the expense of the oxygen contained in the saltpetre. The composition varies in different countries and according to the use to which the explosive is to be put, but generally gunpowder consists of about 75 per cent. of saltpetre, 10 per cent. of sulphur, and 15 per cent. of charcoal. Although in modern times great improvements have been made in gunpowder, the improvements have been of a physical or mechanical and not of a chemical nature. In the manufacture of black powder, the constituents are finely ground, mixed together and the mixture passed through a fine-mesh sieve of copper or brass wire. To secure thorough mixing or incorporation, the mixture, kept in a moist state, is ground in a mill under heavy edge-runners. The cake so produced is broken up into pieces and then subjected to a pressure of, perhaps, 400 lbs. per square inch whereby a hard mass is obtained. The press-cake is then granulated by passage between rollers with pyramidal teeth of different sizes, and the grains polished or glazed in rotating wooden drums into which a small quantity of graphite is sometimes introduced. Finally, the gunpowder is dried by air at a temperature of about 40° C. (104° F.). The violence of the powder as a blasting explosive can be varied by altering the density and size of the grains.

Increase of density and coarsening of the grains make the powder slower.

While still largely used in connection with the beneficent operations of mining and also for pyrotechnic displays, gunpowder is no longer employed as a propellent for military or naval purposes.[1] Its use has been given up not only on account of the large volume of smoke produced in the explosion, which by speedily hiding everything from view prevents the effective use of quickfiring guns, but also because explosives of very much greater power and efficiency have been discovered.

The first great advance in the chemistry of explosives took place with the discovery of *gun-cotton*, in 1846, by CHRISTIAN FRIEDRICH SCHÖNBEIN, Professor of Chemistry in the University of Basle. Cotton consists, essentially, of the chemical substance cellulose, which is, as we have seen (p. 45), a compound of carbon, hydrogen and oxygen. When this is acted on by a mixture of nitric and sulphuric acids, various compounds of cellulose with nitric acid are formed, the composition and properties of which depend on the strength of the acid mixture and the temperature and duration of reaction. The compounds so formed, strictly called cellulose nitrates, are more popularly called *nitro-celluloses*. Since not only cotton but also purified wood fibre or wood pulp and other vegetable fibres consist *essentially* of cellulose, such materials can also be used, and are used, in the production of nitro-cellulose. For the production of explosives cotton is almost exclusively employed, and in its preparation and treatment great care is exercised.

Gun-cotton, which is defined as a nitro-cellulose with more than 12·3 per cent. of nitrogen and not less than 85 per cent. insoluble in a mixture of ether and alcohol (two volumes of ether to one of alcohol), is prepared from cotton linters, or the short fibres which are left after the cotton used for textile purposes has been removed from the cotton seed. The linters, after being freed from dust, are boiled with a solution of caustic soda (sodium hydroxide or NaOH), in order to remove natural oil and non-cellulosic matter, and then bleached. The bleached linters are then opened in a teasing machine and subjected for a period of about two and a half hours to the action of a mixture of nitric and sulphuric acids, an operation frequently carried out in shallow, earthenware pans (Plate 11). After nitration, the waste acid is allowed to run off at the bottom of the pan while water is run on to a perforated plate which rests on the top of the cellulose. The nitrated cotton is then very thoroughly washed and boiled, to render it more stable.

---

[1] It is, however, still used for the bursting-charge of shrapnel, for filling the rings of time-fuses for shells, etc.

Nitration of cellulose is also carried out in closed vessels of stainless steel, and the nitrated cellulose is separated from most of the spent acid by means of a centrifuge.

When ignited, loose gun-cotton burns with great rapidity, but not so rapidly as to constitute an explosion. The molecule of gun-cotton, however, which, as one might say, is almost bursting with energy, is in a very unstable condition, and when subjected to a shock, as, for example, when a little fulminate of mercury or lead azide is caused to detonate near it, it suddenly decomposes and gives rise to a large volume of gaseous substances—nitrogen, oxides of carbon and water vapour. Since these gases are all colourless, and as no solid materials are formed, gun-cotton explodes without production of smoke.

As an explosive, gun-cotton possesses the very important property that it can be used wet. This wet gun-cotton will not take fire when a light is applied to it, but when subjected to the shock of a fulminate of mercury or lead azide detonator, it explodes just as readily as when it is dry. Thus, torpedoes and sea-mines are charged with rolls of moist gun-cotton which have been subjected to a high pressure (six tons per square inch) and so compressed into hard blocks.

The disruptive effect of gun-cotton is very great by reason of the rapidity with which the decomposition of the substance takes place. Thus, whereas a couple of pounds of gunpowder require about a hundredth of a second for complete combustion, the same weight of gun-cotton undergoes decomposition in about one fifty-thousandth part of a second. It is on this fact that the shattering or disruptive effect, the 'brisance,' depends. It is this fact also which makes gun-cotton, which is very valuable as a 'high' or 'disruptive' explosive, unsuitable for use as a 'low' or 'propulsive' explosive in guns. It would simply burst the gun. For effective propulsion, it is necessary to have a rapid and increasing *push* behind the projectile, not an instantaneous increase of pressure.

TUTE OF EDUCATION
Dept. of Extensi
SERVICE.

Although gun-cotton cannot be employed as a propellent, the advantages attaching to a smokeless explosive are so obvious that attempts were made to overcome the difficulties due to the rapid rate of explosion. These attempts to 'tame' the gun-cotton have been entirely successful. Although gun-cotton dissolves only to a slight extent in a mixture of ether and alcohol, nitro-cotton with a lower percentage of nitrogen dissolves completely,[1] yielding a liquid well known under the name of *collodion*, and used under the name of 'newskin' for forming a protective film over cuts. If, then, gun-cotton be mixed with a soluble nitro-cotton and the mixture kneaded with ether-alcohol to form a paste, and if the paste be then granulated by passage through suitable dies, gelatin-like grains are obtained after the ether and alcohol have been removed by volatilization. Such gelatinized nitro-cotton is widely used as a smokeless powder for naval and military purposes in Europe and in the United States of America. It was the first smokeless powder to be used for military purposes. To render the material less liable to undergo decomposition with time, a small amount of a stabilizer, *e.g.* diphenylamine, is incorporated in it.

A further advance in the chemistry of explosives was made by the Swedish chemist, ALFRED NOBEL. When glycerine, which, as we have seen (p. 50), is readily obtained from animal or vegetable fats and oils,[2] is treated with a mixture of nitric and sulphuric acids, it behaves similarly to cotton and yields a substance 'nitro-glycerine,' which is a liquid and very powerful explosive. This substance, discovered by the Italian chemist, SOBRERO, in 1847, and first manufactured on a commercial scale in 1862 by Nobel, was difficult to handle on account of its great sensitiveness to shock, and was the cause of many fatal accidents; but it was found that if the liquid nitro-glycerine was mixed with kieselguhr, a fine earth composed of the siliceous skeletons of marine diatoms, the explosive could be transported and handled with comparative freedom from danger.[3] In this form nitro-glycerine has been extensively used under the name of *dynamite*, its explosion being brought about by means of a fulminate of mercury detonator.

---

[1] The solubility of nitro-cellulose can be greatly altered by treatment, and a nitro-cellulose with high solubility can be obtained from a nitro-cellulose with low solubility by heating the latter with water under pressure.

[2] Glycerine is now produced on a large scale from the oil-refinery gas propylene.

[3] Wood-flour or wood-meal, burnt cork, charcoal and other materials are also used as absorbents in place of kieselguhr.

When about 8 per cent. of nitro-cotton or collodion cotton is mixed with 92 per cent. of nitro-glycerine, a tough jelly-like mass is formed known as *blasting gelatin*. That this explosive is more powerful than dynamite, that it is, indeed, one of the most powerful blasting explosives known, will cause no wonder, since the nitro-glycerine is not mixed with an inactive material like kieselguhr, but with a substance which is itself an explosive. Some of the most commonly used blasting agents are the *gelignites*, formed by adding varying proportions of such materials as potassium nitrate, ammonium nitrate, wood-meal, chalk, to the blasting gelatin.

The British service powder, *cordite*, is prepared by mixing a 'paste' of gun-cotton (65 per cent.) and nitro-glycerine (30 per cent.) with acetone, and adding a quantity of vaseline (5 per cent.).[1] The mixture is then forced by hydraulic pressure through a die into the form of a thread or cord. Hence the name cordite. After evaporating off the acetone, which can be recovered by means of activated charcoal (p. 77), the cordite forms a horn-like material which is very insensitive to shock and safe to handle. The 'taming' action of gelatinization on two of the most powerful explosives is one of the most important and remarkable discoveries in this branch of science; and nitro-cotton, gelatinized in one way or another, is now the basis of all propulsive ammunition.

Although gun-cotton is extensively employed as a high explosive, more especially in torpedoes, other explosives derived from the products of distillation of coal are employed in shells. Of these explosives the two most important and most used are *picric acid* and *trinitrotoluene*.

When phenol (carbolic acid) is treated with a mixture of nitric acid and sulphuric acid there is formed trinitrophenol or picric acid. As ordinarily obtained, it is a faintly yellow crystalline substance, which was long used as a yellow dye for silk. As an explosive it goes by various names, such as melinite, lyddite, dunnite, pertite, and shimosite.

---

[1] Vaseline lowers the temperature of the explosion and so reduces the erosion of the gun-barrel, and it also increases the stability of the cordite when stored.

Picric acid, however, has now been largely superseded by another explosive which is derived from the hydrocarbon toluene, and is called trinitrotoluene, or T.N.T., or *trotyl*. This substance also is a solid, and can be subjected with impunity to very rough usage; a bullet, even, may be fired into the mass without producing any effect. When detonated, however, trinitrotoluene explodes with a violence not much inferior to picric acid, but as the oxidation of the carbon in the compound is by no means complete, dense black clouds of carbonaceous matter are produced. In order to secure more perfect combustion and, at the same time, to reduce the amount of T.N.T. required, ammonium nitrate, a substance containing a large proportion of oxygen, is now generally added. In this way the British service high explosive, *amatol*, a mixture of eighty parts of ammonium nitrate with twenty parts of T.N.T., is obtained. A mixture of T.N.T. and aluminium powder, known as *tritonal*, was used during the war for filling the bombs known as 'block busters.'

The compound *cyclonite*, sometimes referred to as R.D.X., is an explosive which in blasting power and 'brisance' is greatly superior to any other explosive hitherto used for bursting charges. Cyclonite is not produced from coal-tar but from methanol (p. 122), now manufactured mainly from water-gas. By the oxidation of methanol there is produced *formaldehyde* ($H{\cdot}CHO$)—sold in solution as a disinfectant under the name of formalin—which reacts with ammonia to form a compound known as hexamine. By the action of concentrated nitric acid on this compound, cyclonite $(CH_2{\cdot}N{\cdot}NO_2)_3$ is obtained; a compound in which the CH_2 and the $N{\cdot}NO_2$ groups are arranged alternately in the form of a hexagonal 'ring.' A mixture of T.N.T., cyclonite and aluminium powder, known as *torpex*, was used during the war as the most effective under-water explosive for the destruction of U-boats.

It is, one must remember, not merely or even mainly for the purpose of strengthening man's arm in war that explosives have found an application; they have also, through their use in mining and by rendering possible such great engineering works as the Suez Canal and the Panama Canal, and the removal, in 1885, of the reefs known as Hell Gate in the channel of the East River, New York, played an important part in the peaceful progress of civilization. Through the labours of chemists a wide range of explosives has been obtained to satisfy the very varied demands of industry and engineering; and even in the piping times of peace, hundreds of thousands of tons of explosives are produced for rockets and fireworks, and for mining, blasting and sporting purposes (Plates 12 and 13).

Chapter 6

METALS AND THEIR ALLOYS

CHEMISTS are accustomed to classify the elements into metals and non-metals, and this grouping of the elements, although not always sharply defined, is at least convenient. Ordinarily, one thinks of a metal as being opaque and as showing, in the compact state, a lustre, the so-called metallic lustre; and one thinks also of a metal as being a good or fairly good conductor of heat and electricity. These properties serve by no means satisfactorily to define a metal or to distinguish it from a non-metal, but we need not at present trouble ourselves too much about definitions. There are certain familiar substances which are spoken of as metals, such as gold, silver, iron, copper, aluminium, zinc, lead, etc., and it is these substances that will now be discussed.

In our present-day material civilization, metals are of paramount importance in all the activities of life; and there is a constant demand in tool-making, engineering and chemical industry and in connection with transport by rail, road, sea and air, for metals or alloys which combine strength with lightness or which withstand high temperatures and pressures or the corrosive action of liquids and gases.

Microscopic examination has revealed the crystalline structure of metals and experiment has shown how greatly the properties of metals and alloys depend on their crystalline texture and how this may be altered by the mechanical and thermal treatment to which they are subjected.

Certain metals, more especially gold, occur native or in the free state, and it may therefore be supposed that it was with such metals that primitive man first became acquainted. Almost all the other metals, however, occur only in the form of compounds from which the metal must be isolated, and before these metals could be put to use, a knowledge of how they could be extracted from their ores had first to be gained.

The history of the development of human civilization has frequently been divided into three ages or epochs: the stone age, the bronze age and the iron age; and it has been thought that these three periods followed each other successively. This view is in harmony with what is doubtless the case, that copper and bronze were known and widely used before man had become acquainted with iron or had learned how to extract it in quantity from its ores. There was, however, much overlapping of the different 'ages,' and, among certain races, iron was in common use at a time when, among other races, bronze was generally employed. At the present day, one may perhaps say that we are still in the iron (or steel) age, although other metals are, year by year, finding an ever-extending application.

In ancient times, seven metals were known, and as these metals were thought by the alchemists to be affected by and to derive their properties from the planets (including the sun), the names of the planets were applied to the metals which were also represented by the astronomical signs of the planets, as shown in the following list:

Metal	*Planet*	*Sign*	*Metal*	*Planet*	*Sign*
Gold	Sun	☉	Lead	Saturn	♄
Silver	Moon	☾	Tin	Jupiter	♃
Copper	Venus	♀	Quicksilver	Mercury	☿
Iron	Mars	♂			

Traces of these old designations are still met with, *e.g. lunar caustic* (silver nitrate), but of the old names only one remains in use, namely, mercury.

Gold, Silver and Platinum

These three precious metals are widely used for coinage, jewellery and scientific purposes. All occur in the free state, and silver and platinum also occur as compounds associated with other metals.

Gold, probably, was the first metal known, and its natural beauty and the ease with which it can be worked must have attracted primitive man, as it has attracted men throughout all ages, and have led to its use, at an early period, for purposes of personal adornment. The beautiful gold jewellery, bracelets, rings, etc., to be seen in the Museum at Cairo show that the use of gold for ornamental purposes was already well known in Egypt as early as about 3500 B.C.

Gold is very widely distributed, but is produced mainly in South Africa (Transvaal), Russia (U.S.S.R.), the United States of America, and Canada. Although, in the past, much gold was obtained from sands and alluvial deposits, most of the gold is now extracted from gold-bearing rock. This rock, crushed and ground to a fine powder, is treated with a solution of sodium cyanide which dissolves the gold. After filtering off the solid material—from which now uranium may be extracted—the solution is run into large vats, and the gold is caused to separate out by immersion in the solution of a lead-zinc couple. It is then refined.

Gold is a very malleable metal which can be rolled or beaten out into leaves one ten-thousandth of a millimetre (one two-hundred-and-fifty-thousandth of an inch) in thickness, and can also be drawn into wires of extreme tenuity. Gold leaf is translucent and the light transmitted is green in colour.

By electrical heating, gold can readily be fused and vaporized in a high vacuum; and articles of wood, glass, plastic, etc., placed in the evacuated vessel, condense the gold vapour on their surface and thus acquire a 'plating' of the metal. In this way, 'costume jewellery' and other ornamental articles can be produced. Comfort, also, may be obtained by sufferers from eye inflammation by wearing spectacles the lenses of which have been coated, by this vaporization process, with a film of gold of almost molecular thinness. The light transmitted by such lenses is of a cool, green colour and is free from the irritating ultraviolet rays.

The purity or fineness of gold is generally expressed in carats, pure gold having a fineness of 24 carats. Since pure gold is too soft for use (although, we are told, the aborigines of Brazil used it to fashion their fish hooks), it is alloyed or mixed with copper or silver. British currency gold (and also wedding rings) has a fineness of 22 carats, and consists of a mixture of 22 parts of gold with 2 parts of silver and copper, or 91·7 per cent. of gold, 2 per cent. of silver, and 6·3 per cent. of copper. In Australia, silver is used in place of copper. In the United States, currency gold consists of 90 per cent. of gold and 10 per cent. of other metals. In Great Britain four standards of fineness are recognized for jewellery purposes: 22 carat, 18 carat (75 per cent. gold), 14 carat (58·4 per cent. gold) and 9 carat (37·5 per cent. gold). 'White gold,' now much used for jewellery in place of platinum, is produced by alloying gold with palladium or with nickel.

The best solvent for gold is a mixture of nitric and hydrochloric acids—a mixture called by the alchemists, *aqua regia*. A yellow substance, so-called 'gold chloride,' crystallizes from the solution.

SILVER is a metal which also occurs native, more especially in Ontario, Canada; but it is generally found as a sulphide associated with lead or copper, and is produced mainly in Mexico, the United States, South America and Canada. Various methods of a more or less complex kind are employed for the extraction or recovery of silver from its ores.

Silver has long been prized as a jewellery metal on account of its appearance, and was formerly very widely used as a currency metal. For hundreds of years, British sterling silver was an alloy containing 7·5 per cent. of copper, but by 1920, owing to the increase in the price of silver, the amount of this metal in a half-crown (two shillings and sixpence) was worth three shillings and fourpence. In 1927, therefore, an alloy consisting of 50 per cent. of silver, 40 per cent. of copper, 5 per cent. of nickel and 5 per cent. of zinc, was adopted for currency purposes. Now, however, British 'silver coinage' no longer contains any silver at all but is an alloy (cupro-nickel) of 75 per cent. of copper and 25 per cent. of nickel. Sterling silver containing 92·5 per cent. of silver still remains the standard for plate.

Silver does not combine with oxygen at the ordinary or even at higher temperatures and does not, therefore, tarnish when exposed to pure air. The tarnishing which takes place when silver is exposed to the air, especially of large towns, is due to the presence of sulphur compounds in the air and the formation of silver sulphide. This can be removed most easily by liquids containing thiourea (p. 63). The tarnishing of silver may be prevented and its lustre preserved by the electrodeposition of a thin film of the highly reflecting metal rhodium.

Silver is, of all substances, the best conductor of heat and electricity and is used in a number of electrical instruments; and silver, or silver-lined, vessels are used in the brewing and various food-processing industries. The metal dissolves readily in nitric acid but is otherwise not readily attacked by acids or by alkalis. From the solution in nitric acid, white crystals of *silver nitrate*, $AgNO_3$, separate out. This salt is used in the production of light-sensitive silver salts and also in the preparation of *marking inks*.

Owing to the fact that platinum expands and contracts with change of temperature at nearly the same rate as glass, a wire of this metal can be melted into glass and the latter does not crack on cooling. For this reason, platinum wire used to be employed in making connection between the filament of an electric incandescent lamp and the fittings outside. Owing to its high price, however, it is no longer used for this purpose, its place being taken by the nickel-iron alloy, *platinite* (p. 96).

IRON AND STEEL

Highly valued as gold and silver may be for their beauty and for their use as jewellery, and important as the former may be regarded as a basis of values in international exchange, these metals are of small importance in our present-day civilization compared with the metal iron. In the words of Rudyard Kipling:

> '*Gold is for the Mistress—silver for the maid—*
> *Copper for the craftsman cunning at his trade.*'
> 'Good!' said the Baron, sitting in his hall,
> 'But Iron—Cold Iron—is master of them all.'

Yes, master both in peace and in war. We still live in the 'iron age,' and iron constitutes more than 90 per cent. of the world's tonnage of metals.

Although the element iron forms about 5 per cent. of the solid crust of the earth, so far as known, it occurs, with the exception of small quantities of meteoric iron, only in the form of compounds, more especially with oxygen and with sulphur. Of these, the most important are hæmatite (Fe_2O_3), limonite, a hydrated oxide ($2Fe_2O_3$, $3H_2O$), magnetic iron ore (Fe_3O_4), and the sulphide, iron pyrites (FeS_2), the well-known brass-like mineral sometimes called 'fool's gold.' This mineral is never used for the production of iron, but large quantities are employed in the manufacture of sulphuric acid. Various red and brown pigments, *ochres*, are prepared from purified hæmatite and limonite; and different synthetic oxides are produced from waste iron, ranging in shade from yellow to brown and red and purple.

The extraction of iron from its ores (generally the oxide, Fe_2O_3, or the carbonate, $FeCO_3$) is carried out in the *blast furnace*, a tall structure with a roughly egg-shaped interior (Fig. 15). After fires have been lit and the furnace has been heated up, a mixture of ore, coke (or coal), and limestone (calcium carbonate) is introduced from the top and a blast of hot air is blown in through pipes known as tuyeres, or 'twyers' (French, *tuyères*), at the bottom of the furnace. In this way a high temperature is produced; the coke burns and gives rise to carbon dioxide, and this gas in contact with the red-hot coke passes into carbon monoxide, which ascends through the hot mass, combines with the oxygen of the iron ore and so sets free the metal. At the high temperature of the furnace, the metal melts and flows down to the bottom, and at the same time the lime, formed by the decomposition of the limestone, combines with the silicates (clay) added to or present as impurities in the iron ore, to form a glass-like material or slag. This likewise flows in the molten state to the bottom of the furnace, where it floats on the surface of the molten iron. From time to time the slag is removed and the molten iron run off into moulds, where it solidifies and forms *pig iron*.

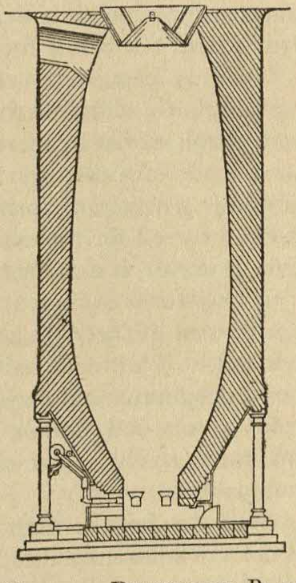


FIG. 15.—DIAGRAM OF BLAST FURNACE

The slag which is obtained from the blast furnace and which has been formed by reaction between the limestone added to the ore and the clay (a hydrated silicate of aluminium) with which the ore is generally associated, is used in the manufacture of *Portland cement*, which consists of a mixture of calcium silicate and calcium aluminate (*Chap.* 9). This cement when mixed to a paste with water has the property of setting to a hard mass even under water, and is therefore of great value for the construction of piers or other engineering works under or in contact with water. The carbon monoxide, also, which escapes in large quantities from the top of the blast furnace is made use of, partly for burning in 'stoves' to heat the air of the blast, and partly for the production of power in gas engines.

Pure iron is never used industrially, and all commercial forms of iron are mixtures of iron with larger or smaller amounts of other substances. The three main kinds of commercial iron are *cast iron*, *wrought iron* and *steel*, and of these, the first is the least pure form of iron. *Cast iron* is essentially the iron as it comes from the blast furnace, and contains generally from 2 to 5 per cent. of carbon, much of it in the form of graphite. The pig iron is remelted and the proportions of carbon, silicon and phosphorus are adjusted so as to give a cast iron suitable for the purpose for which it is to be used—baths, stoves, rain pipes, etc. It is a hard but brittle form of commercial iron.

Ordinary cast iron is readily attacked by dilute hydrochloric and sulphuric acids, but the rate of attack can be reduced to a very remarkable extent by increasing the proportion of silicon. Thus, ware made of a cast iron containing from 12 to 19 per cent. of silicon (*e.g.* tantiron, duriron, ironac, narki) is so acid-proof that it can be used for the evaporation of sulphuric acid. Such cast iron, however, is extremely brittle.

Wrought iron is the purest form of iron used industrially, and is obtained by strongly heating pig iron in a furnace along with hæmatite. This oxide oxidizes the carbon and silicon, as well as any phosphorus and sulphur which may be present. Wrought iron is soft and fibrous in structure, and is also tough and malleable, so that it can readily be worked, even at the ordinary temperature.

Steel, by far the most important form of commercial iron, is not a definite substance; there are many different kinds of steel, all of which are alloys of iron with other substances. Ordinary steels are essentially alloys of iron and carbon, the amount of carbon varying from 0·1 to 2·0 per cent. The carbon is present in the form of a compound with iron known as cementite, Fe_3C.

Steel is produced either by the Bessemer or, generally, by the Siemens-Martin open-hearth process, the aim in either case being to remove, by burning or oxidation, the impurities present in pig iron, and more especially the sulphur and phosphorus, the presence of which is very detrimental to the steel. In the Bessemer process, the oxidation is effected by blowing air through the molten metal, and in the open-hearth process by the addition of oxide of iron or hæmatite. When phosphorus is present in the pig iron, the furnace is lined with magnesite (magnesium carbonate) or with dolomite (double carbonate of calcium and magnesium), with which the oxidized phosphorus combines to form a phosphate known as *basic slag*. This is largely employed as a phosphatic manure in agriculture.

Besides possessing a much greater tensile strength than cast or wrought iron, steel is characterized by the fact that it can be hardened by heating to a fairly high temperature and then cooling in oil or in water. The process is known as *tempering*, and the temper (hardness, elasticity, etc.) produced in the steel depends not only on the composition but also on the temperature to which it is heated and the rate at which it is cooled down. According to the treatment employed, the highly elastic steel of the watch-spring or the hard steel of the cutting tool can be obtained.

The effect of adding other substances to steel has been the subject of intensive investigation by metallurgical chemists, and as a result many new steels possessing distinct and valuable properties have been introduced into the service of man. The addition of chromium, for example, gives hardness to steel, and thus by the addition of about 2 per cent. of chromium one obtains *chrome steel*, which is employed for steel tyres, ball bearings, files, rock-crushing machinery and armour plate. By adding a small amount of nickel to the chrome steel, greater elasticity is given. 'Stainless steel,' which does not rust or tarnish in contact with food or fruit acids, is a steel containing from 12 to 15 per cent. of chromium. It is extensively used for the manufacture of table cutlery. 'Staybrite' steel, containing about 18 per cent. of chromium and about 8 per cent. of nickel, is highly resistant to the corrosive action of sea-water, acids, etc., and is finding increasing use in chemical industry and also for many articles of domestic utility.

Addition of nickel to steel imparts hardness and elasticity, and *nickel steel* is therefore used for armour plate, propeller shafts, etc. When the percentage of nickel is greatly increased, steels having very valuable and special properties are obtained. Thus, *invar*, a steel containing 36 per cent. of nickel and only 0·2–0·5 per cent. of carbon, has a negligible coefficient of expansion throughout the ordinary range of temperature variation. It is therefore used for the manufacture of measuring rods, surveyors' tapes, instruments of precision, and the pendulums of clocks. A similar alloy, *elinvar*, is used for the balance spring of watches, because its coefficient of elasticity and, therefore, the control which the spring exerts, do not alter with the temperature. *Platinite*, similarly, is a nickel steel containing 46 per cent. of nickel. Its coefficient of expansion, which can be varied by slightly varying its composition, is practically the same as that of glass, and so wires of platinite may be sealed into glass. The alloy consisting of 53·8 per cent. of iron, 29 per cent. of nickel, 17 per cent. of cobalt, and 0·2 per cent. of manganese has a coefficient of expansion (4×10^{-6}) almost identical with that of hard glass. This alloy is therefore very useful for sealing into glass for electrical purposes.

When the amount of manganese, which is normally present in small amounts in all steels, is increased up to, say, 9–14 per cent., a very hard, tough steel is obtained, which is extensively used for rock-crushing machinery, switch-points on railways, burglar-proof safes and steel helmets. As this steel is also non-magnetic, it is used in the construction of those parts of ships which are in the neighbourhood of the compass.

As a cutting tool, ordinary high-carbon steel is quite satisfactory so long as the work is carried out at such a rate that the temperature does not greatly rise; but it is useless for the high-speed cutting of metals, when the cutting tool may become red-hot. Under these conditions, ordinary steel speedily loses its hardness. It was, however, found that by the addition of tungsten or of molybdenum to a chrome steel, an alloy was obtained which retained its hardness even at a red heat. Such high-speed tool steel, which contains, say, 0·6 per cent. of carbon, 4 per cent. of chromium, 14–20 per cent. of tungsten (or 5–6 per cent. of molybdenum), and sometimes also about 1 per cent. of vanadium, is therefore a material of the very highest value in modern engineering practice.

When exposed to moist air, iron readily undergoes oxidation or rusts. When used, therefore, in constructional work, protection of the metal by frequent painting is necessary. In other cases the metal may be coated with zinc (galvanized iron), or with tin (tinplate). Corrosion of iron and steel may also be prevented electro-chemically (*Chap.* 10).

COPPER AND NON-FERROUS METALS

COPPER is one of the metals with which man earliest became acquainted; indeed, there is archæological evidence that copper was known almost as early as gold. Its name is derived from the Latin, *aes cyprium*, later *cuprum*, so called because in Roman times it was largely obtained from the island of Cyprus. Hardened by hammering or by alloying with tin to form bronze, copper was used by men of the bronze age for making cutting and other tools, and played an important part in early civilizations.

Although copper occurs native, more especially in the region of Lake Superior, it is mainly from its compounds, the sulphide and carbonate, that the metal is at present extracted. It is produced in large quantities in the United States, Chile, Northern Rhodesia and the Belgian Congo.

The chief industrial use of copper is for the construction of wire and cable for the conduction of electricity; and since the conductivity, which is inferior only to that of silver, is greatly diminished even by small amounts of impurity, the metal, as extracted from its ores, must be refined or purified. This is now carried out by electrolysis, so-called *electrolytic copper* being obtained (*Chap.* 10). For long-span trolley wires and overhead cables, however, where the weight of the cable and stresses due to wind demand greater strength, an addition of 0·9 per cent. of cadmium is made to the copper. Although the conductivity of the copper is reduced by about 10 per cent., the strength of the copper can, by cold-working, be increased by about 50 per cent.

In association with other metals, copper gives rise to a number of alloys, some of which, the *brasses*, find a very widespread use. Brass is an alloy of copper and zinc, and brasses with different properties are obtained by varying the proportions of the two metals. Brasses containing about 30 per cent. of zinc (70/30 brass) are among the most important, and are used for castings and for cartridge cases. A brass containing 40 per cent. of zinc and known as *Muntz metal* is used in sheathing ships on account of its resistance to corrosion.

Dutch metal is an alloy containing about 20 per cent. of zinc. It has a colour resembling that of gold, can be rolled into thin leaf or foil and is used as a gilding metal. The British twelve-sided threepenny piece is a brass consisting of 79 per cent. of copper, 20 per cent. of zinc and 1 per cent. of nickel.

Formerly, steamship condenser tubes were made of 70/30 brass, but an alloy consisting of about 76 per cent. of copper, 22 per cent. of zinc, 2 per cent. of aluminium and 0·4 per cent. of arsenic, has a very much longer life and is now used in most merchant ships.

Brass and certain other alloys which have been subjected to mechanical stress by being hammered, drawn, or pressed, are liable to undergo what is called 'season-cracking.' Thus, hard-drawn tubes, cartridge cases, etc., may crack some time after they have been made, more especially when exposed to an atmosphere in which traces of ammonia are present. This liability to crack may, however, be removed by heating the metal to a temperature of 200° to 300° C. (say 390° to 570° F.). At this temperature the internal stresses are relieved but the hardness of the metal is not destroyed.

Bronzes are, strictly, alloys of copper and tin, but they sometimes also contain zinc. *Gun metal* is a bronze containing from 8 to 12 per cent., and *bell metal* a bronze containing from 12 to 24 per cent. of tin. British 'copper' (bronze) coinage consists of copper 95·5, tin 3 and zinc 1·5 per cent. With 7 per cent. of aluminium, copper forms an *aluminium bronze*, the beautiful golden colour of which reminds one forcefully that 'all that glisters is not gold.' The alloy is used for imitation gold cigarette cases, ornaments and decorative work.

Alloys of copper, nickel and zinc, known as *nickel silvers* (at one time called *German silver*)—*e.g.* copper 54, nickel 24, zinc 22 per cent.—enjoy popularity as a basis for silver-plated ware; and the alloy consisting of copper 54, nickel 45, manganese 1 per cent. is used for decorative and ornamental metal-work under the name of *silveroid*.

For steamship condenser tubes the alloy of copper 70, nickel 28, iron 1, manganese 1 per cent. is superior to that to which reference has already been made, and is used in warships and luxury liners.

Addition of about 2·5 per cent. of *beryllium* to copper increases the tensile strength of that metal six times; and the alloy, nearly as strong as steel, is non-magnetic and does not form sparks when struck. The somewhat rare metal beryllium, associated in the popular mind with the mineral beryl which forms the substance of the gem stones *aquamarine* and *emerald*, promises to become of increasing importance as an alloying metal.

When exposed to the action of moist air, copper becomes coated with a green-coloured, basic copper carbonate, called *verdigris*;[1] and the metal readily dissoves in nitric acid with formation of copper nitrate. *Copper sulphate*, the best known salt of copper, crystallizes from solution in deep-blue coloured hydrated crystals, having the formula $CuSO_4, 5H_2O$. When added even in small amount to water, it prevents the growth of algæ.

A mixture of copper sulphate solution and milk of lime (slaked lime or calcium hydroxide) is largely used, under the name of *Bordeaux mixture*, for spraying fruit trees and bushes, especially vines, to protect them against insect and fungoid pests. This is the main use to which copper sulphate is put.

The metal NICKEL,[2] ores of which occur mainly at Sudbury in Ontario and in Northern Rhodesia, is purified by the Mond process. Carbon monoxide is passed over the crude metal at a temperature of 50° C. whereby a gaseous compound, known as *nickel carbonyl*, is formed. When this gas is heated to a temperature of about 180° C., it decomposes; pure nickel is deposited and carbon monoxide is regenerated, and can be used for the purification of a further quantity of metal. When in a coherent form, nickel is a hard, white, lustrous metal, and is used for the electrodes of sparking plugs for motor-car engines, etc. It is highly resistant to the action of the atmosphere, and for this reason it is used for protecting iron or steel from rust, the metal being deposited by electrolysis (nickel plating). Before being plated with nickel, iron or steel is generally plated with copper.

Nickel is extensively employed as a constituent of many important alloys. Besides the nickel steels, cupro-nickel and the nickel silvers to which reference has been made, one may mention *monel metal* (nickel 68, copper 32 per cent.), which is resistant to corrosion and is used for condenser tubes. Various nickel-chromium alloys, *e.g. nichrome*, are used as resistance heating elements in electric fires and cookers, and for the blades of gas turbine engines.

---

[1] In the neighbourhood of towns, the patina which forms on copper is mainly a basic copper sulphate.

[2] The name *Kupfernickel*, 'rascally copper,' was given by the miners of Saxony in the eighteenth century to an ore from which they had difficulty in extracting copper. When, later, the 'mischievous' ingredient in the ore was isolated, it received the name of nickel.

COBALT.—This metal is well known by name[1] by reason of the beautiful blue colour which its oxide gives to glass and of the pigments prepared from it. The main sources of supply of the metal are the Belgian Congo and Northern Rhodesia.

Cobalt is an important constituent of various alloys used for the manufacture of permanent magnets, being present in these to the extent of 15–35 per cent. It is also a major constituent of alloys, *e.g. stellite* (cobalt, chromium and tungsten) used for the high-speed machining of metals, and of special alloys (*e.g.* cobalt 65, chromium 29, molybdenum 6, iron 1 per cent.) required to withstand high temperatures and used for the blades of gas turbines.

A further use of the metal will be referred to later (p. 104).

CHROMIUM, which, as has been mentioned, forms a constituent of a number of valuable alloys and is now extensively used for the plating of other metals, is obtained by reducing its oxide with aluminium as in the thermit process (p. 42). It is harder than nickel and more resistant to atmospheric action.

MERCURY, the heavy, liquid, lustrous metal, the well-known properties of which lend to it a peculiar fascination, is extracted from the naturally-occurring compound, mercuric sulphide (HgS) or *cinnabar*, a substance which, when ground, yields a powder of a bright-red colour (vermilion). When cinnabar is strongly heated in air, the sulphur combines with the oxygen to form sulphur dioxide, and the mercury is vaporized. By condensing the vapour in cold chambers, the liquid metal is obtained. It is widely used in the construction of thermometers and barometers. Its alloys with other metals are called amalgams. Some of these are used in dentistry.

Mercury gives rise to two classes of salts, known respectively as mercurous and mercuric salts. Mercurous chloride (Hg_2Cl_2) or *calomel* is used in medicine and mercuric chloride ($HgCl_2$) or *corrosive sublimate*, a corrosive poison, is used as a germicide. *Mercury fulminate*, $Hg(ONC)_2$, is used as a detonator.

TIN is one of the metals which were known in ancient times, its alloy with copper constituting one of the earliest known alloys of which we have knowledge, namely, bronze. At least as early as 1000 B.C. the great traders of antiquity, the Phœnicians, obtained this metal from the tin-mines of Cornwall, where it was found in the form of its oxide, known as *tinstone* or *cassiterite*. To this fact is due the old name of Cassiterides or Tin Islands applied to Britain. For a long time the whereabouts of the Cassiterides remained known only to the Phœnicians, and provoked much anxious curiosity on the part of the Romans. So highly, however, was the secret prized that it is recounted that Phœnician sailors, on being followed by a Roman ship while on their way to Cornwall, ran their ship ashore rather than betray the position of the valuable tin-mines.

---

[1] The name is derived from the German word *Kobold* (a gnome or pixy) which was applied by German miners to certain ores which were regarded as worthless—rendered so by the puckish action of the sprites inhabiting the mines. To the metal which was later extracted from the ores the name cobalt was given.

Now the glory of the Cornish tin-mines has departed. More important deposits have in modern times been found in other parts of the world, chief amongst these being those at Perak and Selangor (Malay States), in Bolivia, Nigeria, Siam, and in the islands of Banca and Billiton in Indonesia. Only a small amount of tin is now mined in Cornwall.

Tin is a metal of manifold uses. Its resistance to atmospheric attack has led to its use for coating iron and steel as a protection against rusting. Tinplate, used for making containers, 'cans' or 'tins,' for biscuits, preserved foods, etc., is made by dipping steel sheets in molten tin, and also by electrodeposition of tin. About half the world's production of tin is now used for making tinplate.

Tin is very malleable and can be rolled out into thin foil which is extensively used in electrical condensers and as a wrapping material for chocolates and other materials. So-called *silver paper* is not silver at all, but the much less valuable metal tin.

In association with other metals tin forms part of a number of alloys. Thus there are known *bronze* (copper and tin); *Britannia metal* and the *Babbitt metals* (tin, antimony and copper) used for bearings of engines; *pewter* and *solder* (tin and lead). *Tinsmith's solder*, which is required to solidify rapidly to its maximum strength, contains 60–65 per cent. of tin. *Plumber's solder* contains only half this proportion of tin and becomes pasty during solidification owing to the separation of crystals of lead. This behaviour makes the solder suitable for 'wiping' into shape.

Except during the warmer summer months, ordinary lustrous tin, or white tin, is not in a really stable condition, but at all temperatures below 13° C. (about 55° F.) is liable to undergo change and pass into a less dense form known as grey tin. At ordinary temperatures this change takes place with extreme slowness, and may, indeed, not take place for centuries; and the change is retarded by the presence even of traces of bismuth, lead, antimony and cadmium. At very low temperatures, however, and even during severe winters in European countries, the change may occur with considerable rapidity, and is accelerated by traces of aluminium, zinc, cobalt and manganese. Generally, the conversion of white to grey tin takes place in spots or patches, and owing to the lower density of grey tin, wartlike powdery growths are formed, the appearance of which on the surface of the bright metal has earned for the transformation the name of *tin plague*. This 'plague,' moreover, is contagious, for the conversion of white tin to grey tin is stimulated and accelerated by contact with the latter. All articles of tin—organ pipes, medals, pewter pots, etc.—are liable to suffer from tin plague, and the results may sometimes be disastrous (Plate 15).

ZINC occurs in many countries, mainly in the form of its sulphide, known as zinc blende, some of the most important deposits being found in the United States, in British Columbia and at Broken Hill, Australia. The zinc is generally associated with other metals in the ore, so that this has first to be subjected to a process whereby the zinc ore is concentrated. The zinc concentrate is then treated for the extraction of the metal, which in the crude state is known as spelter.

Zinc is a bluish-white metal, the main uses of which are for the production of brass and for galvanizing iron. It is also used in the construction of Leclanché and dry cells. An alloy of zinc and aluminium (about 4 per cent.) is extensively used in the production of a great variety of articles from toys to door handles and from clothes wringers to radiator grilles and carburetters for motor cars. The articles are frequently nickel or chromium plated.

Oxide of zinc is used in surgical dusting powders and ointments and as a pigment under the name of *zinc white*; and a mixture of zinc sulphide and barium sulphate is employed as a pigment under the name of *lithopone*.

LEAD is a heavy metal which has been known and used from the earliest times and which also finds wide application at the present day. Owing to its resistance to atmospheric attack and to the action of acids, this metal is employed for roofing purposes, for sulphuric acid plant, for lining vats in which chemical processes are carried out, for sheathing electrical cables, etc. It is also extensively used in the manufacture of storage batteries. Lead is so plastic that it can be extruded, under pressure, through dies into the form of rods and pipes, and lead pipes have been used from very early times for the conveyance of water. Water containing carbon dioxide in solution attacks lead fairly readily, but this action is checked by the presence of carbonates or sulphates of calcium and magnesium. Since these salts are present in what is called 'hard' water (*Chap.* 9), it follows that hard water attacks lead to a much less extent than distilled or than a soft moorland water. Owing to the fact that lead in solution is poisonous, the resistance of this metal to the action of water is of great importance in connection with the use of lead pipes for the conveyance of drinking water. Where the water of a town's supply is very soft, it is necessary to 'harden' it somewhat by the introduction of small quantities of lime.

Lead hardened by the addition of a small amount of arsenic is used in the manufacture of shot, and lead hardened by the addition of antimony finds use as *type metal.* Alloys of lead, tin and bismuth, or lead, tin, bismuth and cadmium, are used as *fusible metals*, some of which melt considerably below the boiling-point of water. They are used for various safety devices, fire alarms, automatic fire extinguishers, boiler safety plugs, etc.

Lead combines with oxygen to form a number of oxides, the most important of which are *litharge* (PbO), *red lead* (Pb_3O_4) and *lead dioxide* (PbO_2). Red lead is extensively used in the production of 'crystal' glass (*Chap.* 9), as a plumber's cement, and as a pigment, *minium.* Lead dioxide forms the material of the positive plate of the lead storage cell (*Chap.* 10).

Another very important compound of lead is *white lead*, a so-called basic carbonate of lead having the composition, $2PbCO_3$, $Pb(OH)_2$. For the production of this pigment, litharge or lead sponge, which is readily oxidized to litharge, is treated with a solution of lead acetate, and a solution of basic lead acetate is formed. Into this solution carbon dioxide is passed, and basic lead carbonate or 'white lead' separates out as a white powder.

TITANIUM.—Although white lead is valuable as a pigment on account of its covering power, it suffers from the disadvantage that when exposed to air containing sulphuretted hydrogen, it becomes dark owing to the formation of black lead sulphide. The white pigment, *titanium white* (titanium oxide), which has a high opacity, does not darken in sulphurous air and has a lower density than white lead, is now largely used.

Titanium metal is found to improve the properties of a number of alloys, even when present in relatively small amount. It is now coming into increasing use for constructional purposes as it combines strength with lightness and has a high resistance to corrosion.

TUNGSTEN, which is obtained from the mineral wolfram, is a metal which fuses at the very high temperature of 3382° C. (6119·6° F.). It finds a very widespread use in metal-filament electric lamps. On account of its diamond-like hardness, *tungsten carbide* (a compound of tungsten and carbon) is superior to tungsten steel for high-speed cutting tools. A mixture of tungsten carbide with 10–20 per cent. of cobalt is pressed, ground to the desired shape and heated to a high temperature. A material known as *carboloy* is formed, the cobalt serving as a matrix which holds the tungsten carbide in position. This material is used for tipping cutting and drilling tools.

GERMANIUM is a rare metal which, in recent years, with the development of electronics, has found special and important applications. The metal, which occurs in very small amount in certain coals and is recovered from the flue-dust of power stations, is used in what are called transistors—tiny pieces of apparatus for amplifying minute currents of electricity. These transistors can perform most of the functions of the radio valve and are much simpler in construction.

Four other metals, sodium, potassium, aluminium and magnesium, which are produced electro-chemically, will be discussed in *Chap.* 10.

Chapter 7

VELOCITY OF REACTIONS AND CATALYSIS

THE overthrow of the phlogiston theory by Lavoisier towards the end of the eighteenth, and the enunciation of the atomic theory by Dalton early in the nineteenth century, marked the beginning of a new era in chemical science. After that time, the activities of chemists were directed in an increasing degree to the preparation and to the quantitative determination of the composition of new substances and naturally occurring materials, as well as also to the determination of the atomic weights of the elements. Moreover, the study of the compounds of carbon, a branch of science to which the name of Organic Chemistry is applied, began to be developed with an ever-increasing energy; and in this domain, the problems connected with the constitution of the molecule, that is, with the arrangement of the atoms within the molecule, were so important for the proper understanding of the enormous array of substances which chemists were able to prepare, that such questions exercised, and very properly exercised, a powerful fascination over the workers in that branch of chemistry. The quite wonderful results which were thereby obtained not only had a value in the domain of theoretical chemistry, but led also to some of the most brilliant achievements of practical chemical science—to the preparation of dyes, drugs, perfumes, and many other materials of the greatest industrial and, one may say, human value—so that one need not hesitate to regard such work as amongst the most important in the whole history of the science.

By the workers who achieved such splendid success, chemical reactions were regarded entirely or mainly from the material point of view, from the point of view of the substances undergoing change and of the substances produced by the change. But there is clearly another aspect of the subject which demands attention. Just as we have already recognized that substances are carriers of energy, and that a chemical reaction or chemical change is a mode of transforming chemical energy into other forms of energy, so also in modern chemistry one is concerned not merely with the material *products* of chemical change, but also with the *process* of chemical change itself. Why does a chemical reaction take place, and what are the laws governing the rate at which and the extent to which a chemical reaction proceeds? These are the questions which *chemical dynamics*, one of the most important branches of modern chemistry, seeks to answer.

Although it is not possible to discuss the subject fully here, the attempt must be made to give some indication of the more general principles in order that one may gain a better appreciation of present-day chemistry and a more intelligent understanding of some of the most recent and economically most important industrial processes, the development and success of which depend on dynamical investigations.

When, in the thirteenth century, the great Dominican monk and Bishop of Regensburg, ALBERTUS MAGNUS, used the word 'affinitas,' he merely summed up the views current at that time, that chemical reaction is due to a similarity or kinship between the reacting substances. But although this term affinity or chemical affinity is still in use, it must now be regarded not as signifying any natural resemblance or family relationship, but rather as a force, electrical in nature, which acts between different kinds of matter and which, under certain conditions, brings about a chemical action between them. The existence of this force is postulated in order to account for the fact that chemical change or reaction will take place between substances when thereby potential energy can be converted into work. Chemical affinity, it should be noted, does not give an *explanation* of chemical change; it is, rather, a measure of the work done by a system when it undergoes change.

One of the most important factors in the process of chemical change is the speed with which it takes place, the velocity of the reaction. That there are great differences in the rates at which chemical change occurs is so obvious as almost to render its emphasis unnecessary. The rusting of iron, the oxidation of aluminium, the burning of wood, the explosion of gun-cotton, are chemical changes which take place with markedly different velocities. This great difference in the rate of reaction we shall be inclined to attribute to differences in the chemical affinity, and in so doing we shall be right, but only partly right; for when one studies the process of chemical change more fully, it is found that the rate of a reaction does not depend merely on chemical affinity, but also on a number of other factors. Of these factors, one of the most important is the *concentration* of the reacting substances, that is, the amount of the substances in a given volume. We shall be able to understand this more readily if we fix our attention, for the present, on reactions between gaseous substances. When a substance is in the state of a gas, its molecules are supposed, according to the kinetic theory (*Chap.* 11), to be moving about with great velocity in all directions, and combination or reaction between two substances, A and B, can take place only when molecules of A and B collide or come within each other's sphere of influence. If, then, we have a certain number of molecules of the substance A and a certain number of molecules of B moving about in a given space, an A molecule will collide with a B molecule a certain number of times per second, and the rate of reaction, therefore, will have a certain value. Suppose that the number of B molecules is now doubled. It is clear that in the same unit of time an A molecule will now have double the number of chances of colliding with a B molecule and of entering into reaction with it, and the rate of reaction will therefore be twice as great as it was originally. Similarly, if the concentration not only of the B molecules, but also of the A molecules be doubled, then it is clear that the rate of reaction will again be doubled; that is, the reaction now takes place four times as fast as it would have done with the original concentrations of the two substances. The speed of a reaction, in fact, is proportional to the product of concentrations of the reacting substances. This law of the dependence of the speed of a chemical change on the concentrations of the reacting substances was discovered by two Norwegian scientists, GULDBERG and WAAGE, and is generally known as the *law of mass action.*

The velocity of chemical change is also very greatly influenced by the temperature, a fact to which we have already alluded (p. 37). Although the speed of different reactions is affected in a different degree by temperature, it may be taken as a convenient approximation that the speed of a reaction is doubled by raising the temperature 10° C. (18° F.). A simple calculation will show what the magnitude of this effect may be. Suppose that a reaction requires one second for its completion at the melting-point of ice, that is at 0° C. (32° F.). At 100° C. (212° F.), the boiling-point of water, the same change would take place in about one-thousandth of a second; and if we raise the temperature but a little more, say to 200° C. (392° F.), the time required for the change will now be only about one-millionth of a second. On the other hand, a change which would require one second to take place at 200° C., would need, at 0° C., a period of a million seconds, that is, about eleven and a half days. This influence of temperature is of the greatest importance, and on its recognition may depend the success of an industrial process.

A further very important result which has followed from the dynamical study of chemical reactions is the recognition of the fact that chemical changes are reversible, and that the direction in which reaction between different substances takes place depends not merely on chemical affinity but on the relative concentrations of the different substances. When steam (oxide of hydrogen) is passed over heated iron, oxide of iron and hydrogen are produced.[1] On the other hand, when hydrogen is passed over heated oxide of iron, steam (oxide of hydrogen) and metallic iron are formed.

$$\left\{\begin{array}{l}\text{Iron}\\ \\ \text{Oxide of hydrogen}\end{array}\right. \quad \rightleftarrows \quad \left.\begin{array}{r}\text{Iron oxide}\\ \\ \text{Hydrogen}\end{array}\right\}$$

In the former case, the steam is present in large abundance, whereas the hydrogen which is formed is swept away and cannot, therefore, react with the oxide of iron. In the latter case, the hydrogen is present in abundance, and the water vapour is carried away in the stream of gas and so is prevented from reacting with the metallic iron. By altering the relative concentrations of the steam and the hydrogen, therefore, one can cause reaction to take place in whichever direction one pleases. Suppose, now, that the experiment is arranged in such a way as to prevent the removal of the hydrogen or of the steam, as can be done by heating all four substances together in a closed vessel, then it will be found that both reactions will take place; steam will react with iron, and hydrogen will react with oxide of iron, so that finally a state of balance or *equilibrium* will be produced, at which there will be a certain definite relationship between the concentration of the steam and the concentration of the hydrogen.

---

[1] This is one of the processes used for the industrial production of hydrogen.

So long as the temperature is kept constant, the same state of balance or equilibrium will be reached, no matter what may be the initial amounts of hydrogen and of steam, but if the temperature is altered, the state of equilibrium will, in general, also be altered. By raising or lowering the temperature the one or the other reaction can be caused to take place to a greater and greater extent, and the direction in which the equilibrium is thereby altered is found to be intimately associated with the heat effects which accompany the chemical change.[1]

The discovery of the laws of chemical change, and the recognition that, theoretically at least, all reactions are reversible, mark one of the most important advances in our knowledge of chemical processes and of the action of chemical affinity. Some of the consequences which flow from this will be discussed in the sequel.

Although, as has been said, the progress of a chemical reaction and the rate at which a chemical change proceeds are influenced both by the concentration of the substances and by the temperature, it is found that the velocity of a chemical reaction may also be profoundly affected in another way which, on account of its very great importance both in the laboratory and in the factory, demands fuller consideration.

In the early decades of last century a number of phenomena were observed which, although isolated and apparently unconnected, all possessed one common characteristic, namely, that the rate at which a chemical change took place was markedly increased by the addition of certain substances in minute, sometimes in almost infinitely minute, amount. Owing to such additions, it was found, substances which seemed under the particular conditions to be without action on each other, reacted with appreciable, sometimes even with great, readiness. From the magnitude of the result produced, it was evident that the foreign substance could not enter into the reaction in the ordinary way; but, as the Swedish chemist, BERZELIUS, pointed out, the substance which was added appeared to act merely by its presence and by 'arousing the slumbering affinities of the substances,' and so allowing them to react. How these slumbering affinities were aroused, Berzelius did not hazard a guess, but in order to give a name under which such phenomena could be classed, he introduced, in 1838, the term *catalysis* (a word which signifies a loosening); and a substance which brings about catalysis is called a 'catalytic agent' or a 'catalyst.' For long the phenomenon of catalysis, of which the number of cases observed rapidly increased during the nineteenth century, was regarded by chemists, as Gulliver was regarded by the learned men of Brobdingnag, as a *lusus naturæ*; it was relegated to the realms of the mysterious, and chemists became only too prone to think that the label of catalysis was at the same time an explanation of the phenomenon. It was, indeed, only towards the end of last century and owing to the development of the experimental methods of measuring the rate of chemical change, that the phenomenon of catalysis and the behaviour of catalysts began to form the subject of systematic investigation. With the main characteristics of catalysis and the behaviour of different catalysts, we must now become acquainted.

---

[1] The law which is found to obtain here can be stated in a simple form. It will be clear that if one reaction is accompanied by an evolution of heat, then the reverse reaction must be accompanied by an absorption of heat. *When the temperature is raised, the reaction accompanied by absorption of heat is favoured, whereas lowering the temperature favours the reaction which takes place with evolution of heat.* Only when no heat effect accompanies chemical change is the equilibrium unaffected by change of temperature.

As has already been indicated, one of the most striking features of catalysis is the magnitude of the effect produced, compared with the small amount of the substance producing it. An excellent illustration of this is seen in the influence which moisture exercises on the rate of combination of gaseous substances. When hydrogen and oxygen, the two gaseous substances by whose combination water is formed, are heated together, they combine, and if the temperature is sufficiently high, say about 600° C. (1112° F.), the combination takes place with explosive violence. But this occurs only when a trace of moisture is present in the gases. If the last traces of moisture are removed from the gases by prolonged contact with the substance known as phosphorus pentoxide (obtained by burning phosphorus in air), a substance which combines with the greatest avidity with water, the mixture of hydrogen and oxygen can then be heated even to a temperature of nearly 1000° C. (1832° F.) without explosion occurring. Not only in the case of hydrogen and oxygen, but in the case also of many other gases, combination is found to depend on the presence of moisture, of which, however, the merest trace suffices.

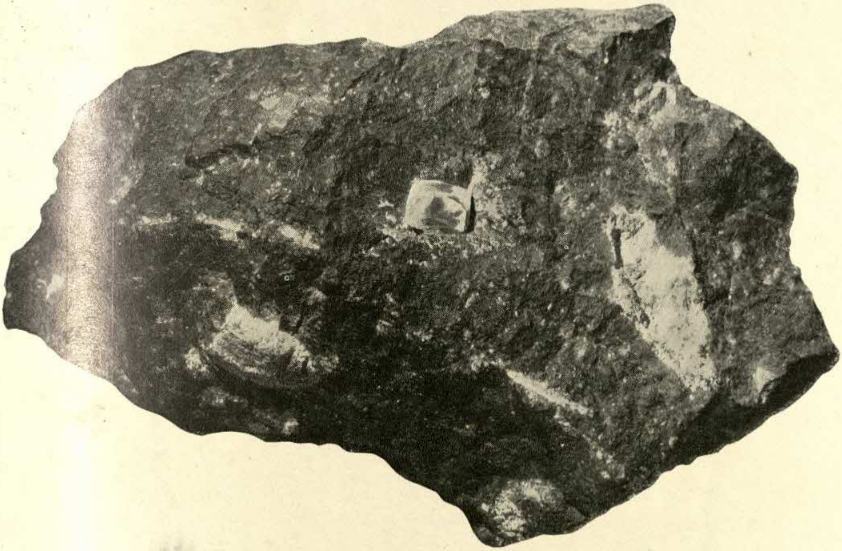
This action of moisture, and, indeed, the action of catalysts generally, has been likened to the action of oil in the bearings of a machine; a catalyst diminishes, as it were, the hindrances to change of whatever nature these may be without itself being used up in the process.

In astronomy one deals with magnitudes so vast as to be beyond the grasp of our minds; in the domain of catalysis the magnitudes are, in some cases, so small that it becomes almost equally impossible to form a true conception of them. In order, however, that the reader may have some knowledge of the very minute amounts of substance which will yet suffice to affect appreciably the speed of a reaction, let me give one example out of the many which might be chosen. When one dissolves sodium sulphite (Na_2SO_3) in water, the oxygen of the air slowly oxidizes the sodium sulphite to sodium sulphate (Na_2SO_4). By the addition of certain catalysts, the speed with which this process takes place can be greatly increased, and in this connection copper has been found to be very efficient. In fact, if only one grain of copper sulphate is dissolved in 1,400,000 gallons of water, or one grain in about 250,000 cubic feet of water, the presence of the copper can be detected by its action in accelerating the oxidation of the sodium sulphite! Even water which has remained in contact with metallic copper for three-quarters of a minute contains sufficient copper to show a noticeable effect. One is, however, so accustomed to judge of the importance of a thing by the amount of space it occupies that in asking the reader to recognize the infinite importance of the infinitely small and to accept the example I have given, sober fact of science as it is, I am almost afraid that I shall be considered as putting too great a strain on his credulity.

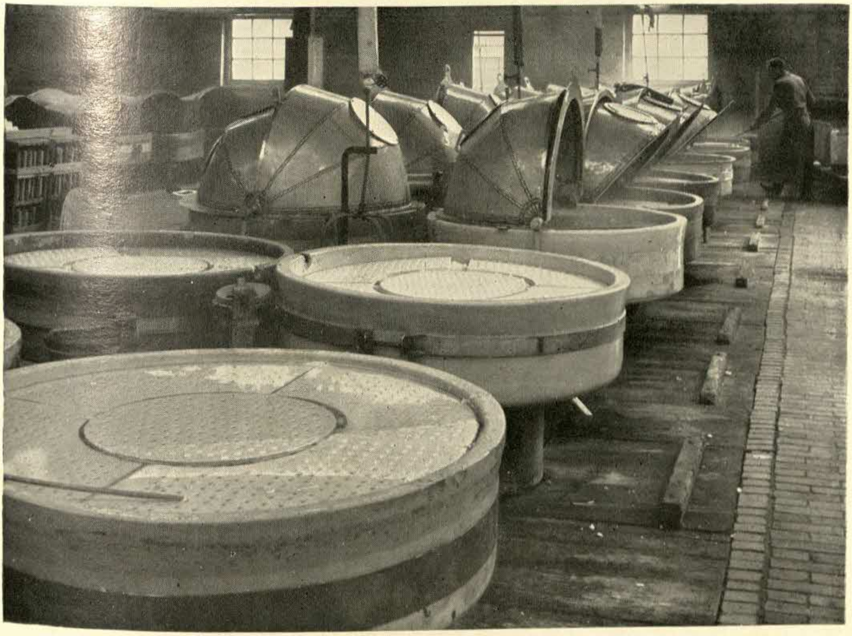
Not only may catalysts increase the velocity of a chemical change, they may also decrease it. That is, we may have *negative* as well as *positive* catalysis. The oxidation of a solution of sodium sulphite by oxygen is, as we have learned, accelerated by copper salts, but it is *retarded* by tin salts; and it is retarded also by certain alkaloids, *e.g.* nicotine. Even a puff of tobacco smoke (containing nicotine) through the solution of sodium sulphite produces a detectable retardation of the oxidation. The occurrence of negative catalysis is frequently of great importance because it becomes possible to retard processes of decomposition and so to stabilize a substance by means of suitable catalysts. Thus, certain explosives are stabilized by diphenylamine (p. 82); and the oxidation process which causes rubber and silk to 'perish' can be greatly retarded by means of thiourea, $CS(NH_2)_2$, and other substances.

Catalysis may occur not only in homogeneous but also in heterogeneous systems, as when solid substances act as catalysts in gaseous and liquid systems. Thus, if the case of hydrogen and oxygen be again considered, it is found that although combination of the two gases takes place at high temperatures with explosive velocity, at the ordinary temperature no trace of combination can be detected. If, however, a little metallic platinum be brought into contact with the mixture of the two gases, combination proceeds with appreciable velocity; indeed, if the platinum is used in a finely divided form, known as platinum sponge or platinum black, the rate of combination may be so great, and the amount of heat evolved so large, that the platinum is heated to incandescence and ignites the mixture. An explosion results. This action of platinum, one of the first cases of catalytic action to be observed, brings out very clearly two of the main characteristics of the phenomenon, namely, the great change produced in the speed of the reaction, and the fact that the catalyst remains unchanged in amount. The same piece of platinum can be used to bring about the combination of unlimited quantities of hydrogen and oxygen.

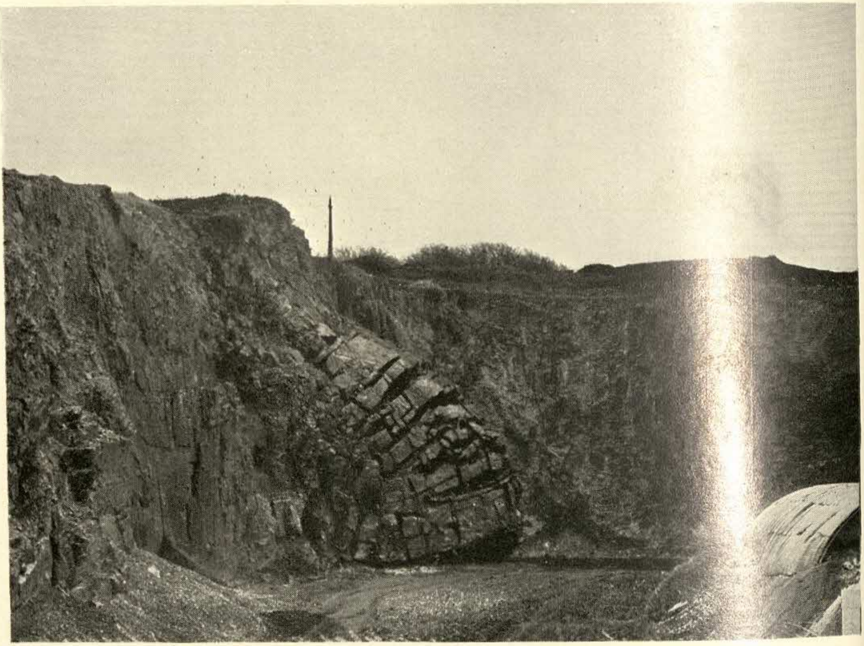
This remarkable behaviour of finely divided platinum, which greatly impressed, as well it might, the minds of the early observers, was not long in receiving a practical application. In 1823 it was observed by a German chemist, DÖBEREINER, that if a jet of hydrogen is allowed to impinge on a piece of spongy platinum exposed to the air, the heat of combination of hydrogen and oxygen raises the platinum to incandescence and the hydrogen becomes ignited. Döbereiner, therefore, constructed an apparatus in which hydrogen was produced by the action of sulphuric acid on zinc; and when a tap was opened the gas escaped in a fine jet and impinged on a piece of spongy platinum.



10. A 20-CARAT CAPE DIAMOND EMBEDDED IN BLUEGROUND



11. PANS FOR NITRATING CELLULOSE



12. BLASTING ROCK IN A QUARRY

13. BLASTING ROCK IN A QUARRY

In this way fire could be obtained, and, as a matter of fact, this Döbereiner lamp was widely used for that purpose before the days of matches.

Platinum acts as an effective catalyst for the decomposition of hydrogen peroxide into water and oxygen, and is used for this purpose in certain engines (p. 68).

Although platinum is by no means a universal catalyst for all reactions—no such universal catalyst is known—it has nevertheless been found that platinum acts very generally as a catalytic accelerator of oxidation reactions, or reactions in which gaseous oxygen takes part. Oxide of cerium, which forms a small part of the Welsbach incandescent gas mantle (p. 71), also acts as a catalyst and accelerates the combustion of the coal-gas.

Platinum sponge, used in automatic gas lighters, may, after some time, lose its catalytic activity, owing to certain substances present in the gas. This destruction of the catalytic activity, this 'poisoning' of the catalyst, as it has been called, is a phenomenon of the greatest importance, the recognition of which has been, as we shall learn more fully presently, not only of scientific interest, but also of the greatest industrial importance.

By chemists the importance of catalysis is now fully recognized, and the systematic search for the most suitable and effective catalyst for a given reaction is a well-established part of chemical investigation; but it is part of the romance of science that discoveries of value are made not only as the result of consciously directed effort, but also by the aid of 'that power which erring men call Chance.' And in this connection the following tale may be retold, for it illustrates not only the special action of a catalyst, but also the important rôle which catalysts may play in industry.

For the preparation of a certain dye—it was a dye called sky-blue alizarin, but the name does not matter—the necessary ingredients were heated for some time in a vessel made of iron. In the course of time fresh apparatus had to be installed; and with this apparatus no sky-blue alizarin was obtained, but something entirely different. What could be the reason for the failure? The process was carried out in the same way as before, and the workmen were the same, or were under the same direction. The apparatus, certainly, was new, but it was exactly the same as the old apparatus. And yet, no; it was not exactly the same. The new apparatus, instead of being entirely of iron, had a copper lid. But surely that could not be the cause of the different behaviour. Yet so it was, for the small trace of copper derived from the lid exerted, it was found, a powerful catalytic influence on the course of the reaction, and instead of the substances reacting so as to form sky-blue alizarin, a further reaction took place which gave rise to a totally different substance.

It might perhaps seem as if the tracing of the trouble to its source would finish the story, but this is by no means the case. Accident had thrown a catalyst for a new reaction in the way of the chemist, who, by careful investigation, found that a trace of copper enabled the ingredients used, as well as a number of other similar substances, to react in a particular manner, and in this way *a new and important series of dyes was discovered.* It all seems very simple; all a matter of 'happy accident.' But was it by a happy accident that the cause of the trouble in the first instance was discovered? Or was it a happy accident that converted a source of trouble in one process into a source of gain in another? How would the matter have stood without the trained intelligence of the chemist with his knowledge of the importance of little things, with his trained faculty of observation and his ability to make use of the facts which he observed?

Important as are the phenomena of catalysis in pure science and in industry, they are, literally, of much more vital importance in the animal and plant organism.

The animal organism is like a laboratory in which numerous reactions and marvellous transformations take place unceasingly —the transformation of the food consumed into the bone and flesh and blood of the body, and the slow combustion of the tissues to yield the energy and heat necessary for vital activity. And so it is also with the plant organism in which there takes place the building up or *synthesis*, not only of the complex materials which serve as foodstuffs for the animal creation, but also of those sweet-smelling essences and the compounds which give to flowers their varied odours and colours. Many of these substances, the products of Nature's laboratory, can also be made in the laboratory of the chemist, and their synthesis from simple inorganic materials constitutes the crowning achievement of chemical science. But how different are the methods of the chemist from those of Nature. In his laboratory the chemist makes use of high temperatures and the action of powerful and corrosive reagents; but in the laboratory of Nature, the building up of even the most complex compounds takes place quietly and smoothly at the ordinary temperatures. All this the animal or plant organism accomplishes by utilizing appropriate catalysts, accelerators of reactions, the so-called *enzymes*, which are themselves produced within the living cells of a plant or animal. The ptyalin of the saliva, the pepsin of the gastric juice, the trypsin of the pancreas, the diastase of the sprouting barley-corn, the zymase of the yeast, which has from time immemorial been used by man for the conversion of sugars into alcohol—these are some of the numerous catalytic agents which Nature produces and of which she makes use in her marvellous achievements in chemical synthesis. Not only do enzymes play an indispensable rôle in the economy of Nature, but they are also being made to play a part of ever-increasing importance in industry, as we shall learn more fully later (*Chap.* 15).

In the manufacturing industries it may truly be said that time is money; and to produce an article of manufacture at a more rapid rate is the same as saving time. And this is just exactly what a catalyst enables one to do. It is, therefore, not surprising that in almost all branches of chemical industry the value of catalysts has become increasingly recognized, and that, by their introduction, new industries of the highest importance have been established, and older industries have been revolutionized. It would, in fact, be no exaggeration to speak of the present as the catalytic age in chemical manufacture. Although reference has already been made to the industrial application of catalysts (*e.g.* in the hydrogenation of coal and production of oils, p. 57), a little space may appropriately be devoted here to the discussion of a few other important reactions in which catalysis has found industrial application. In succeeding chapters, other applications will be discussed.

MANUFACTURE OF SULPHURIC ACID

Sulphuric acid, or oil of vitriol (H_2SO_4), the discovery of which dates from the fifteenth century, is one of the most important substances in our modern civilization. It is used in the production of superphosphate and ammonium sulphate; in the refining of petroleum; for cleaning or 'pickling' steel plates previous to tinning and galvanizing; in electrical storage batteries; in the manufacture of rayon, dyes, explosives and many other industrial products. Although in a number of industries, such as the production of superphosphate, hydrochloric acid and ammonium sulphate, changes have taken and are taking place which make the use of sulphuric acid less necessary, production of the acid has gone on increasing.

The reaction on which the production of sulphuric acid depends is the oxidation of the gas sulphur dioxide (SO_2), to form the compound sulphur trioxide (SO_3), which combines readily with water to give the compound known as sulphuric acid. The difficulty is met with, however, that combination between sulphur dioxide and oxygen does not take place appreciably at the ordinary temperature; and when one seeks to hasten the combination by raising the temperature, another difficulty is encountered. As the temperature is raised the rate at which the sulphur dioxide and the oxygen combine certainly increases, as we have already learned to be universally the case, but as the temperature rises the *extent* to which combination takes place becomes less and less, by reason of the fact that at high temperatures the sulphur trioxide decomposes again into sulphur dioxide and oxygen. The result, therefore, is that at a temperature at which the combination of sulphur dioxide and oxygen would take place sufficiently rapidly, the amount of sulphur trioxide formed is too small to allow of the process being commercially successful. We now know, however, the direction in which to look for a way out of the difficulty. We must find a catalyst which will so accelerate the rate of oxidation of the sulphur dioxide that the process may be carried out with sufficient rapidity at a temperature so low that the decomposition of the sulphur trioxide is negligible. Such a catalyst was found at an early date in the oxides of nitrogen, nitric oxide (NO) and nitrogen dioxide (NO_2); and since the year 1746 the manufacture of sulphuric acid has been carried out by a process depending on the use of these oxides. Sulphur dioxide, together with air and oxides of nitrogen, is passed into a series of large lead chambers into which also a fine spray of water is injected. Here the nitric oxide combines with the oxygen of the air to form nitrogen dioxide which then transfers the oxygen to the sulphur dioxide so as to form sulphur trioxide. This combines with water to form sulphuric acid. There is thus an alternate oxidation of the nitric oxide to nitrogen dioxide and reduction of the latter by the sulphur dioxide with re-formation of nitric oxide.

This cycle of reactions serves to explain the action of a catalyst, in a number of cases at least. Just as it is easier to ascend a steep hill by a series of gentle gradients rather than by the steeper direct path, so a catalyst may facilitate (accelerate) a reaction by offering the possibility of a cycle of reactions which readily occur, in place of a single direct reaction which takes place with difficulty—or not at all.

The acid produced in this 'lead chamber process,' as it is called, contains about 65 per cent. of sulphuric acid (H_2SO_4), and must be subjected to processes of purification and concentration before the pure acid is obtained.

At the beginning of the present century another process began to come into prominence. This was due mainly to the successful development of the process of manufacture of synthetic indigotin (*Chap.* 13), which necessitated the use of the very powerful reagent obtained by the addition of sulphur trioxide to pure sulphuric acid, and known as fuming sulphuric acid or 'oleum.'

As far back as the year 1817, it was suggested by Sir HUMPHRY DAVY that platinum sponge might be employed to accelerate the oxidation of sulphur dioxide by oxygen, just as we have seen that this metal accelerates the combination of hydrogen and oxygen; and in 1831, practical application of this suggestion was made by a vinegar manufacturer of Bristol, PEREGRINE PHILLIPS by name. Great hopes were aroused for the success of this method of manufacturing sulphuric acid, but a period of nearly seventy years elapsed before the discovery of Peregrine Phillips was developed into a successful industrial process.[1]

When the attempt was made to utilize the 'contact process,' as it is called, for the commercial production of sulphuric acid, a difficulty was met with which delayed success and threatened complete failure. The production of sulphur trioxide which at first took place with great readiness soon began to diminish, and after some time ceased altogether. The platinum lost its catalytic activity. On investigation, this loss of activity was found to be due to a 'poisoning' of the platinum—a phenomenon to which we have already referred—and the substance which was found to be chiefly responsible for this was arsenic. This arsenic was derived from a small amount of impurity contained in the iron pyrites, a naturally occurring sulphide of iron used as the source of the sulphur dioxide, and it was only after much labour that a means was found of ridding the gas of all traces of this poison. When this had been done, the contact process could be carried out with success.

---

[1] On a restricted scale, Squire and Messel, in England, manufactured oleum by the contact process, from 1875 onwards. They obtained the sulphur dioxide by the combustion of sulphur or by the decomposition of sulphuric acid on hot brick surfaces.

For the production of sulphuric acid by the contact process, the enormous lead chambers, with a capacity sometimes of 150,000 cubic feet, are replaced by comparatively small, cylindrical vessels containing a suitable catalyst. For this purpose, compounds of vanadium are in widespread use. At a temperature of about 450° C. (say 840° F.), oxidation of the sulphur dioxide takes place rapidly and practically completely, and the sulphur trioxide issues from the apparatus as a white mist, which is then passed into a solution of sulphuric acid containing about 98 per cent. of acid. In this way a pure sulphuric acid, as well also as the powerful fuming sulphuric acid (called 'oleum'), to which we have referred, can readily be obtained.

The *sulphur dioxide* required for the production of sulphuric acid may be obtained by heating iron pyrites (sulphide of iron, FeS_2) or spent oxide of iron from the gas-works (p. 63) in a current of air, or by burning sulphur in air. It is also formed in large amounts as a by-product in the smelting of copper and zinc sulphide ores and in the manufacture of cement from anhydrite (calcium sulphate). When anhydrite is heated with sand (silica), clay and coke, sulphur dioxide is evolved; and the clinker which is left in the furnace and which consists of a mixture of calcium silicate and calcium aluminate forms, when ground, *Portland cement*. This process is being increasingly developed in England as a source of supply of sulphur dioxide for the manufacture of sulphuric acid.

SULPHUR has been known from very early times, and the fumes of burning sulphur (sulphur dioxide) were used for fumigation and 'to drive away foul fiends and evil spirits.' Although mainly a product of volcanic activity sulphur is also being produced at the present day under favourable conditions (*e.g.* in brackish lakes in the Sudan) by bacterial decomposition of existing sulphates. The element occurs free over an extensive area in Sicily and also forms great underground deposits in the State of Texas, in the delta of the Mississippi and elsewhere. As these deposits cannot be mined in the ordinary way, a nest of concentric tubes is inserted in a borehole and water, heated under pressure to about 160° C., is passed down to the sulphur-bearing stratum. The sulphur is thereby melted and the molten sulphur is forced to the surface by hot compressed air passed down through the central pipe.

Sulphur is a substance of great importance for it is used not only for the production of sulphuric acid but also as a raw material in chemical industry, in the vulcanizing of rubber, as a fungicide and for other purposes. As demand threatens to outrun supply, it is important that waste of this element should be avoided and new sources of supply developed.

In some countries, elemental sulphur is being produced from iron pyrites which occurs abundantly and widely distributed in nature. When pyrites is heated out of contact with air, part of the sulphur distils off and can be collected; and if the pyrites is then roasted in a current of air the remainder of the sulphur is obtained as sulphur dioxide. From this the sulphur can be recovered by passing the gas through coke at a temperature of about 1000° C. The coke reduces the sulphur dioxide with formation of sulphur and carbon dioxide. Similarly, elemental sulphur can be recovered from the sulphur dioxide produced in the various processes referred to above, in so far as the dioxide is not required for the production of sulphuric acid or for other purposes.

From hydrogen sulphide, also, which is present in coke-oven gas and sometimes also in large amount in natural gas, and which is produced in the refining of petroleum, sulphur can be obtained by controlled combustion or by passing the gas with air over a catalyst. The hydrogen sulphide is thereby oxidized to water and sulphur is set free.

It may be that at some future time, also, sulphur will be produced commercially from sulphates by microbiological processes.

HYDROGENATION OR HARDENING OF OILS

Another important industry which depends on the application of catalysis is that of the conversion of liquid oils into solid fats; a process referred to as the hydrogenation or hardening of oils.

It has already been pointed out (p. 50) that the animal and vegetable fats and oils are, essentially, compounds of glycerine with acids, such as palmitic, stearic and oleic acids. The glycerine compounds of the saturated palmitic and stearic acids are solid, and constitute the main portion of the hard fat, beef suet. The glycerine compound of the unsaturated oleic acid is, however, a liquid, and is the chief constituent of olive oil; and the other natural animal and vegetable oils are also mainly compounds of glycerine with unsaturated acids. For these different fats and oils there are, at the present day, two main uses: namely, as foodstuffs, to supply the body with the necessary amounts of carbonaceous matter, and for making soap. So far as foodstuffs are concerned, butter, or the fat of milk, constitutes a large part of the fatty material consumed. Owing, however, to the increase of population and to the rising price of butter, the problem of obtaining some substitute for this very important article of diet became of increasing importance. The solution of the problem we owe to French ingenuity, and the industrial production of butter substitutes, *e.g. margarine*, which dates from 1870, has now attained to very great dimensions. Beef-fat or hog's lard, after being melted and clarified, is mixed in churning machines with various vegetable oils, such as cotton-seed oil, soya-bean oil, coconut oil, palm-kernel oil, and also with milk. The milk is added in order to emulsify the fats and also to confer flavour, the flavouring properties being developed by the addition to the milk of bacteria which bring about the production of lactic acid. Although the margarine so obtained is an efficient substitute for butter so far as the supply of energy is concerned, it is lacking in certain important food accessories, to which the name of *vitamins* (*Chap.* 16) has been given. This defect is now remedied by the addition to the margarine of vitamins A and D, obtained partly by synthesis and partly from fish-liver oils; and vitaminized margarines are now put on the market certified to contain these vitamins in as high a proportion as they are contained in the best butter.

Since these butter substitutes are derived mainly from animal fats, the supply of solid fats necessary for the manufacture of soap was seriously diminished; and it became, therefore, a matter of great importance to discover a method by means of which liquid oils could be converted into solid fats. Theoretically, the process is a simple one. Oleic acid, for example, differs from stearic acid only in the fact that it contains less hydrogen. It is what has been called an unsaturated compound, and if the oleic acid is combined with the proper amount of hydrogen, it is converted into the solid stearic acid; or, on the other hand, if hydrogen is combined with the liquid glycerine oleate, the solid fat, glycerine stearate, is obtained. Similarly with the other unsaturated compounds present in other oils. Although it was not difficult to carry out such a conversion in the laboratory, no commercially successful process was discovered until it was found that finely divided nickel acts as an efficient catalyst. In the presence of this metal, the liquid oils, olive oil, linseed oil, whale oil, etc., combine with gaseous hydrogen and become converted into solid fats suitable for use in the manufacture of soap and for the preparation of edible fats. This important industrial application of catalysis is based on the purely scientific investigations of the French chemists, PAUL SABATIER and JEAN BAPTISTE SENDERENS, carried out at the beginning of the present century.

Not only does the introduction of this process offer to the soap-boiler a fresh source of the material which he requires, but it also permits of the profitable employment of substances for which formerly comparatively little use could be found. Thus, for example, whale oil, which on account of its unprepossessing taste and smell found formerly but little application, is now converted in large amount, by the process mentioned, into a solid, odourless material suitable for the making of soap.

This result has led to a great expansion of the whaling industry. The introduction of the hydrogenation process, moreover, will, by stimulating the cultivation of oil-producing plants, *e.g.* ground nuts and soya beans, exercise a profound influence on the economic development of those countries which are suitable for such cultivation. Of the importance in the service of man of this modern industrial hydrogenation process, founded as so many industrial processes are on investigations of apparently purely scientific interest, it is impossible to form an estimate.

SYNTHESES FROM WATER-GAS

Mention has been made of the fact that the action of catalysts is largely specific, and it is found that by a proper choice of catalyst and regulation of the conditions of reaction, the same substances may be made to react in various ways. No better illustration of these statements could be obtained than what is offered by the numerous products which can be obtained from the mixture of carbon monoxide and hydrogen, known as water-gas. This mixture, we have seen, is the basis of the Fischer-Tropsch process, and from it hydrocarbons can be produced which are not only of great value as fuels and lubricants, but which, in the hands of chemists, have also been made to yield a great array of materials which are of service to man.

Formerly, practically all the *methyl alcohol* or *methanol*, which is used in large amount as a solvent and in the manufacture of formaldehyde, dyes, perfumes, etc., was produced by the distillation of wood; but since 1925, a large and rapidly increasing proportion has been produced by a catalytic process founded on researches carried out mainly by French and German chemists. When a mixture of carbon monoxide and hydrogen is passed over a suitable catalyst (*e.g.* zinc chromite), under regulated conditions of temperature and pressure, the two gases combine to form methyl alcohol or methanol, CH_3OH, as shown by the equation, $2H_2+CO=CH_3OH$.

From a mixture of carbon monoxide and hydrogen, also, by the use of different catalysts and by suitable variation of the conditions of temperature and pressure, *butyl alcohol*, C_4H_9OH, a valuable solvent for nitro-cellulose lacquers and a raw material for the production of butadiene (*Chap.* 14), can be obtained.

Further, very large amounts of water-gas are used at the present day as a source of industrial hydrogen. Although the hydrogen may be separated from the carbon monoxide by a process of liquefaction and distillation, similar to that used in the case of liquid air, a catalytic method is mainly employed. Thus, when water-gas and steam, at a temperature of about 500° C. (say, 930° F.), are passed over a catalyst consisting essentially of iron oxide, the carbon monoxide reacts with the steam to form carbon dioxide and hydrogen. The carbon dioxide is then easily removed by dissolving in water under pressure. If a mixture of water-gas and producer-gas is used with steam, a mixture of nitrogen and hydrogen, suitable for use in the production of ammonia, is obtained. Carbon dioxide is, of course, also formed in the process.

A mixture of carbon monoxide and hydrogen is obtained not only when steam is passed over red-hot coke but also when methane and steam are passed over a catalyst of nickel and aluminium at a temperature of about 900° C. (say, 1650° F.): $CH_4+H_2O=CO+3H_2$. This reaction has become of great importance as it can also be used as a means of obtaining cheap hydrogen for the hydrogenation of coal—methane being one of the by-products of the process.

Chapter 8

CHEMISTRY AND AGRICULTURE

ALTHOUGH agriculture has been practised from time immemorial, it is only in comparatively recent years that a more exact knowledge has been obtained of soil fertility and plant growth. As early as 1563, the view was clearly stated by the French potter, BERNARD PALISSY, that dung was applied to the land in order to replace something which the growing crop had removed, although, early in the following century, the Belgian chemist, JEAN BAPTISTE VAN HELMONT, concluded that water is the sole nutrient of plants. 'I took an earthen vessel,' records van Helmont, 'in which I put 200 pounds of soil dried in an oven, then I moistened with rain water and pressed hard into it a shoot of willow weighing 5 pounds. After exactly five years the tree that had grown up weighed 169 pounds and about 3 ounces. But the vessel had never received anything but rain water or distilled water to moisten the soil when this was necessary, and it remained full of soil, which was still tightly packed, and, lest any dust from outside should get into the soil, it was covered with a sheet of iron coated with tin but perforated with many holes. I did not take the weight of the leaves that fell in the autumn. In the end I dried the soil once more and got the same 200 pounds that I started with, less about two ounces. Therefore the 164 pounds of wood, bark and root arose from the water alone.'

The experiment was simple but the conclusion, although it seemed to be convincing, was nevertheless incorrect, for van Helmont had omitted to take account of two factors—the carbon dioxide and water vapour in the air and the salts which had been removed from the soil; for, as we have already learned, the green leaves of plants take in carbon dioxide and water vapour and, absorbing the radiant energy of sunlight, transmute these substances into sugar, starch and cellulose. In the erroneous conclusion drawn by van Helmont we have a warning of the care which must be exercised in the performance of a scientific experiment and in the interpretation of the results.

Although it had long been known that plants contain inorganic constituents which appear in the ash when the plant is burned, it was the German chemist, Justus von Liebig, who first, in 1840, gained definite acceptance of the view that plants do not subsist merely on the water and carbon dioxide which they abstract from the air and the soil, but that they have also to be fed with the elements necessary for the building up of their structures. No fewer than about thirteen elements are required by plants, and of these, the most important, apart from carbon and hydrogen, are nitrogen, phosphorus and potassium; and these must be present in the soil in the form of salts or soluble compounds which can be taken up by the plants. One ton of wheat, it is stated, abstracts from the soil 47 pounds of nitrogen, 18 pounds of phosphoric acid and 12 pounds of potash. So long as the population of the world was comparatively small, the great tracts of virgin soil contained an ample supply of the necessary mineral salts to secure crops adequate for the feeding of the people; and although the efficacy of dung in increasing the crop was well known, and although such manure was applied, the farmer had little to do but till the soil and sow the seed. Owing to exhaustion of the soil, however, and to the great increase of population which has taken place in modern times, it has become necessary to increase the yield of the soil by the addition in larger and larger amounts of the inorganic salts necessary for the life and growth of food plants. Although some of the fertilizers which are now indispensable for intensive agriculture are found ready-formed in Nature, yet in the economic exploitation of these natural deposits, in rendering them suitable for absorption by the plant, and in the artificial production of fertilizers in ample amount and at lower cost, we may recognize one of the greatest services which chemists have rendered to man. Since, moreover, the nature and amount of the different fertilizers to be used depend on the plant, soil and climatic conditions, chemical knowledge and investigation are necessary for the production of a properly balanced fertilizer.

While it is a matter of the highest importance that agriculturists should have at their command adequate supplies of the essential fertilizers, it is also important to bear in mind that a deterioration of the soil may occur if artificial, inorganic fertilizers alone are used, and if attention is not paid to the renewal of the

OF EDUCATION FO
Dept. of Extension
SERVICE.

store of organic humus in the soil. This humus can be renewed by the addition to the soil of leaves, vegetable waste, straw, farmyard manure, etc., which have been allowed to rot or undergo change under the action of bacteria. Seaweed, also, may profitably be brought into service; and the ploughing up and reseeding of old grasslands may also be used for the effective renewal of humus. Through the loss of humus, brought about by intensive cultivation and by the sole use of artificial fertilizers, the soil structure is destroyed and soil fertility and quality of the crops may be impaired. Serious erosion, also, may take place owing to the soil becoming less permeable to and being washed away by rain. Artificial fertilizers, therefore, must be made use of with knowledge and understanding.

The addition of POTASSIUM SALTS to the soil is of great importance because such salts give health and vigour to the plant, and make the leaves more efficient in utilizing the energy of sunlight and more efficient producers, for example, of sugar and starch. In root crops, therefore, there is a greater storage of food material and the roots become larger. Potassium salts are of importance for the cultivation, more especially, of potatoes, beet and fruit crops, and the banana plant responds in a most surprising fashion when manured with salts of potassium (Plate 16).

When land vegetation is burned, the potassium which the plants had taken from the soil is recovered in the ash in the form of potassium carbonate (K_2CO_3). This salt was formerly obtained by lixiviation of the ash with water, evaporation of the solution and calcination of the residue in pots. Hence the name *pot-ash* given to potassium carbonate. For long, the potash so obtained constituted the main source of supply of this salt, and in the middle of last century nearly three-quarters of the world's supply came from the wood ashes of the Canadian lumber camps.

At the present time, nearly all the potassium salts used are of mineral origin. Until the period between the two World Wars, they were obtained mainly from the great salt deposits which are found in the neighbourhood of Stassfurt, in Germany; and in these deposits the chief potassium salts are *sylvine* (potassium chloride), *kainite* (a double sulphate containing not only potassium but also magnesium) and *carnallite* (a double chloride of potassium and magnesium).

Now, however, deposits of potassium salts are also being worked in France, Russia, Spain, Canada, and the U.S.A., expecially in Texas and near Carlsbad in New Mexico. Very large amounts of potassium salts are also being extracted from the brine of Searles Lake in the Mojave Desert, California; from the water of the Dead Sea; and from the flue-dust of cement works (Plate 17).

In England, borings near Eskdale in Yorkshire have proved the existence of large deposits of sylvinite (potassium chloride with sodium chloride) at a depth of some 4,000 feet. The problem of how these deposits can be exploited economically has, however, not yet been solved.

That PHOSPHATES are necessary for healthy plant growth has been known since the end of the eighteenth century, and their importance, more especially for cereals and pasture, became more fully appreciated in later years. In countries with a low rainfall, phosphates are of especial value in increasing and strengthening the crop and also in accelerating the processes of growth and ripening. They are of great value also in improving the feeding value of crops, especially of pastures, so that, by their application, grass land may be greatly improved and may be made to carry more stock.

Before the year 1840, phosphorus was added to the soil chiefly in the form of crushed bones, the phosphorus being present as calcium phosphate, the calcium salt of phosphoric acid. Between 1840 and 1850, however, JOHN BENNET LAWES, founder of the Agricultural Experimental Station at Rothamsted in Hertfordshire, showed that the phosphate could be rendered more readily soluble in the soil and therefore more readily available for the plant, by treating the ground bones with sulphuric acid. The so-called normal calcium phosphate, $Ca_3(PO_4)_2$, is thereby converted into acid calcium phosphate, $CaH_4(PO_4)_2$, with production at the same time of hydrated calcium sulphate or *gypsum*. To the mixture of acid calcium phosphate and gypsum the name *superphosphate* was given.[1] Soon thereafter, deposits of mineral rock (phosphate rock) were discovered, and from this nearly all superphosphate is now produced. About 30 per cent. of the world's supply of mineral phosphate comes from the enormous deposits in French North Africa, and about 50 per cent. from America.

---

[1] Phosphate rock may also be treated with nitric acid, whereby a combined phosphatic and nitrogenous fertilizer can be obtained.

By treating calcium phosphate with phosphoric acid one obtains the soluble acid calcium phosphate, without admixture with gypsum. This contains nearly three times as much phosphoric acid as does ordinary superphosphate, and is used as a fertilizer under the name of *triple superphosphate*.

Ground *basic slag* (p. 95) is also used, in large amount, as a phosphatic fertilizer, more especially for the treatment of grazing land. It is of importance because it contains, besides phosphorus, small amounts of other elements, *e.g.* magnesium and manganese, which are essential to plants.

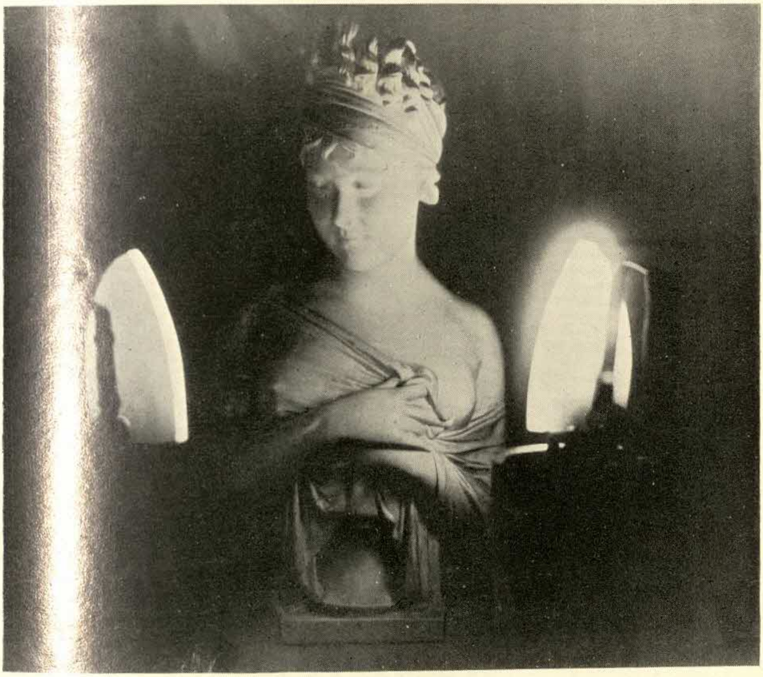
In various countries, the production of another phosphate fertilizer is being developed. When phosphorus is heated to a high temperature with steam, phosphoric acid is formed and hydrogen is liberated. The hydrogen is used, as we shall learn presently, for the production of ammonia, and the ammonia is then combined with the phosphoric acid to form ammonium phosphate ('di-ammon-phos'), which may be used both as a phosphatic and as a nitrogenous fertilizer.

Of the different fertilizers used in agriculture the most important are those which feed the plant with *nitrogen*, for it is on such fertilizers that increased crop production, in countries with a not too low rainfall,[1] mainly depends. More especially is this the case with wheat and other cereals. Although it has been found that leguminous plants (peas, beans, lucerne, clover, etc.), through the symbiotic action of colonies of bacteria occurring in nodules on the roots, are able to take up and assimilate elementary nitrogen from the air, most plants are unable to do so; and combined nitrogen must, therefore, be added to the soil in a form which the plants can assimilate (Plate 18).

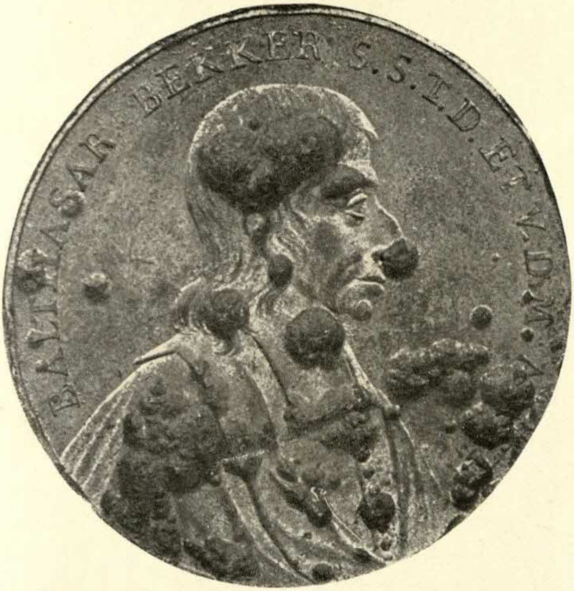
Owing to the apparent impossibility of coaxing the enormous store of elementary nitrogen contained in the air into suitable combination with other elements, mankind contented itself, resignedly if not complacently, with the natural sources of supply of useful nitrogen compounds; and this position was all the easier to adopt as the natural supply was sufficient for the

---

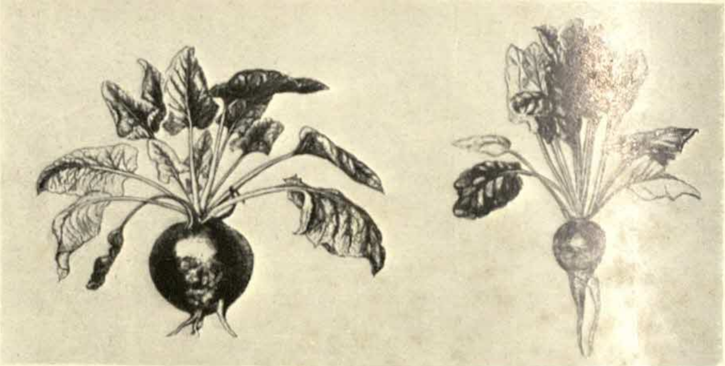
[1] Where the annual rainfall is less than about 20 inches, nitrogenous fertilizers do not produce large increases in crops. In such countries phosphate fertilizers are specially important.



14. PHOTOGRAPH TAKEN BY INFRA-RED LIGHT

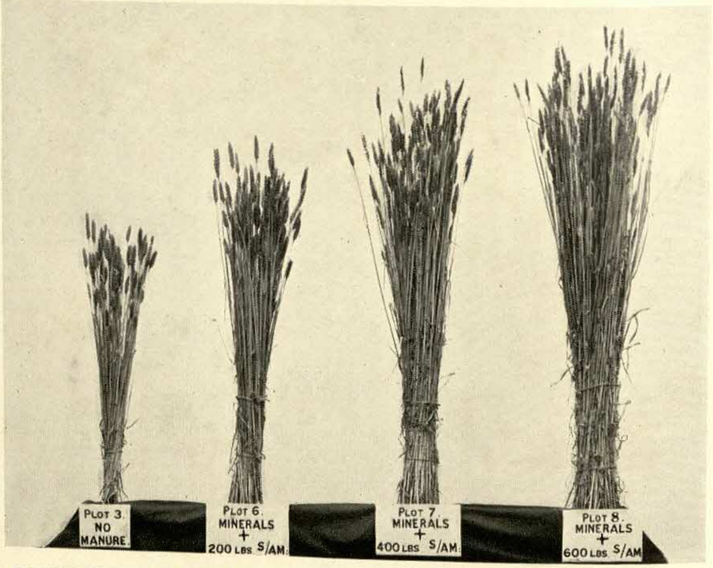


15. MEDAL SHOWING TIN PLAGUE



16. EFFECT OF POTASH SALTS ON THE GROWTH OF MANGOLDS
The root on the left has been grown in soil to which a complete fertilizer has been added; that on the right, in a soil containing no potash

17. SEARLES LAKE, CALIFORNIA
Below the crust of salts there lies a saturated brine from which potassium chloride, borax and other salts are extracted


PLOT 3. NO MANURE
PLOT 6. MINERALS + 200 LBS S/AM.
PLOT 7. MINERALS + 400 LBS S/AM.
PLOT 8. MINERALS + 600 LBS. S/AM

18. EFFECT OF NITROGENOUS FERTILIZERS (AMMONIUM SULPHATE) ON PLANT GROWTH

needs of the day. In 1898, however, Sir WILLIAM CROOKES, as President of the British Association, delivered the solemn warning that the years of plenty were quickly passing. The supply of wheat, the staple foodstuff of Western peoples, from all the land available for cultivation, would soon be insufficient to provide for the needs of the growing population unless the yield of the soil could be greatly increased by intensive cultivation; and this in its turn would, in a few years, exhaust all the known sources of combined nitrogen. Famine, therefore, stared them in the face, and there would be no Egypt from whose granaries supplies could be obtained.

Apart from waste animal and vegetable matter, which was quite inadequate in amount and, in some cases, had only a local importance, agriculture depended for its supply of nitrogenous fertilizers mainly on the ammonia produced as a by-product in the distillation of coal, and on Chile saltpetre or sodium nitrate. Although coal was a valuable source of supply of combined nitrogen, it was not economically practicable to produce from it an adequate supply of nitrogenous fertilizer. Moreover, although it was possible greatly to increase the production of Chile saltpetre, the nitrate deposits, although very large, were not inexhaustible, and might, it was thought, become exhausted within the lifetime of a generation.[1] It is clear, therefore, that the situation in 1898 was one which might well cause grave concern to men of foresight and scientific knowledge; and Sir William Crookes was only doing his duty in calling the attention of his countrymen and of the world to the inevitable disaster which threatened unless some fresh means were found of obtaining combined nitrogen.

As the discovery of any considerable new supplies of naturally occurring nitrogen compounds was scarcely to be relied on, there was an imperative demand laid on chemists to discover some means of forcing the inexhaustible store of elementary nitrogen into such a state of combination that its assimilation by plants would be rendered possible. As Sir William Crookes said: 'The fixation of atmospheric nitrogen is one of the greatest discoveries awaiting the ingenuity of chemists.' And the ingenuity of chemists, assisted by the engineers, has proved itself equal to the task. Since about 1903, not one but several methods have been discovered by means of which the atmospheric nitrogen can, on a large scale and in a commercially successful manner, be forced into useful combination with other elements. Indeed, so far as nitrogenous fertilizers are concerned, the prospect of a wheat famine has now been removed to an indefinitely remote future.[1]

---

[1] It now seems probable that the Chile saltpetre deposits will suffice to supply world needs for many years to come.

(1) *Direct Combination of Nitrogen and Oxygen*

Since the atmosphere consists essentially of a mixture of nitrogen and oxygen, it is obviously most natural that attempts should be made to bring about the combination of these two gases, the possibility of which had been proved by the experiments of Cavendish in 1785 (p. 25).

The industrial production of nitric acid and nitrates from atmospheric nitrogen and oxygen was commenced in Southern Norway in 1903 and was carried on successfully for about twenty-five years. The process required an abundant supply of cheap electricity and was abandoned, about 1926, in favour of the production of synthetic ammonia from nitrogen and hydrogen (p. 131).

(2) *Fixation of Nitrogen by means of Carbides*

In 1906, another process was introduced for the fixation of atmospheric nitrogen, which depended on the use of calcium carbide, a compound manufactured in large amount for the production of acetylene. When nitrogen is passed over this carbide, suitably heated in retorts, a reaction takes place with formation of a compound known as calcium cyanamide ($CaCN_2$), and the production at the same time of a quantity of carbon. The dark-grey coloured mixture which is thus obtained, and which contains about 60 per cent. of calcium cyanamide, is put on the market under the name of *nitrolim*, or *lime nitrogen*, as it is called in America.

For this compound, calcium cyanamide, quite a number of uses were developed, but the most important was its use as a source of nitrogen in agriculture. When properly applied to the soil, calcium cyanamide was found to have a fertilizing value for cereals nearly equal to that of ammonium salts. The physical qualities of the commercial nitrolim, however, its dustiness and dirtiness, were prejudicial to its use, and although the former defect has been largely removed, much of the cyanamide is used, not directly as a fertilizer but for conversion into ammonium salts, ammonia being readily obtained by passing superheated steam over the cyanamide.

---

[1] The great increase which has taken place, *e.g.* in Canada, in the production of cereals, and notably of wheat, is not due entirely to the increased use of nitrogenous fertilizers. By the application of plant genetics it has been possible to produce improved varieties of wheat which are resistant to disease (*e.g.* rust) and which will grow under adverse conditions of drought and shortness of season.

(3) *Production of Synthetic Ammonia*

However important might be the processes to which reference has already been made, they could not, on account of their dependence on cheap electric power, furnish a complete solution of the 'nitrogen problem.' The announcement, therefore, in 1912, that the direct combination of nitrogen and hydrogen to form ammonia had been developed into a commercially successful process was recognized as of the highest significance and importance.

The problem of successfully bringing about the direct combination of nitrogen and hydrogen is one which had taxed the ingenuity of chemists for many years. Inert as the two gases are towards each other at the ordinary temperature, it was well known that by the passage of electric sparks through a mixture of the two gases, ammonia is produced, but only in very minute amount. It was, moreover, also known that when electric sparks are passed through gaseous ammonia, decomposition, almost but not quite complete, into nitrogen and hydrogen takes place. In other words, it was known that the reaction between nitrogen and hydrogen is a reversible one, and leads therefore to a state of equilibrium; but the concentration of ammonia present is exceedingly small, and all attempts to obtain an appreciable amount of the compound by direct combination of nitrogen and hydrogen ended in failure. New weapons, however, were being forged, the weapons of chemical dynamics, and with these the problem was again attacked. In 1912, as the result of ably directed and painstaking endeavour, the problem was solved.

Experiment has shown that when nitrogen and hydrogen combine, the volume of the ammonia produced is less than that of the mixed hydrogen and nitrogen; and therefore, according to the laws of chemical dynamics, the relative amount of ammonia produced will be increased by bringing the gases together under a high pressure. Moreover, combination of nitrogen and hydrogen takes place with *evolution* of heat; and therefore (p. 109, footnote) the formation of ammonia will be favoured by keeping the temperature *low*. The following table shows how the predictions of theory were borne out by experiment:

Temperature	*Percentage amount of ammonia in the equilibrium mixture when the pressure was*	
	1 atmosphere	100 atmospheres
800° C. (1472° F.)	0·011	1·1
700° C. (1292° F.)	0·021	2·1
600° C. (1112° F.)	0·048	4·5
500° C. (932° F.)	0·13	10·8

In order, therefore, to attain success in the industrial synthesis of ammonia from its elements, the rule must be borne in mind: Maintain the gases under as high a pressure and at as low a temperature as possible.

But here again we meet with that factor which so sharply distinguishes success in the scientific laboratory from success in the factory, the factor of time. At about 500° C., it is true, quite an appreciable amount of ammonia is formed by the direct combination of hydrogen and nitrogen, but the rate at which this amount is produced is so slow that the process would be industrially useless. Again, therefore, the first immediate requirement is the discovery of a suitable catalyst, and such a catalyst was found in osmium, in uranium, in iron, and in certain other substances, some of which previous investigators had also employed, but without achieving success. And here again, as in other cases to which reference has been made, failure was due to a non-recognition of the fact that catalysts can be 'poisoned.' Through the presence of minute traces of different impurities in the nitrogen or hydrogen, the efficiency of the catalyst can be destroyed, and it was only by laborious and careful investigation of the behaviour of different catalysts, and of the behaviour of other substances towards these catalysts, that success was made possible. Nor indeed were the engineering difficulties much less than the chemical, but they were all overcome, and the production of synthetic ammonia was added to the industries of the world. In the economic utilization of Nature's boundless store of nitrogen, therefore, catalysts play an all-important part.

In the manufacturing process, first successfully achieved by the German chemist, FRITZ HABER, and often spoken of as the Haber process, a mixture of nitrogen and hydrogen, under a pressure of 150–200 atmospheres, is circulated, by means of a pump, over the catalyst[1] heated to a temperature of about 500° C. (932° F.). After passing over the catalyst, the gases, which now contain a certain proportion of ammonia, are washed with water, so as to dissolve the ammonia, while the unchanged nitrogen and hydrogen are made to circulate again over the catalyst.

A number of modifications of the original Haber process have been introduced, of which the two most important are the Claude (French) and the Casale (Italian) processes. These differ from the Haber process mainly in the fact that they operate under very much higher pressures.

For use as a nitrogenous fertilizer, ammonia is converted into ammonium sulphate. Formerly, this salt was obtained by combining the ammonia with sulphuric acid, but now use is very extensively made of anhydrite ($CaSO_4$). If a suspension of finely ground anhydrite in water is treated in a closed vessel with ammonia and carbon dioxide,[2] ammonium sulphate and calcium carbonate are formed, as indicated by the equation:

$$CaSO_4 + H_2O + 2NH_3 + CO_2 = CaCO_3 + (NH_4)_2SO_4$$

The calcium carbonate can then be used for the production of cement (p. 163), or as a liming agent in agriculture. Mixed with ammonium nitrate it is used as a fertilizer under the name of *nitro-chalk*.

As a consequence mainly of the development of the synthetic ammonia process, the position of the nitrogen industry has undergone a very remarkable change. Not only has the total production of nitrogen compounds greatly increased in recent years, but the amount produced by the industrial fixation of atmospheric nitrogen now greatly exceeds the amount contributed by Chile saltpetre and by the distillation of coal. This fact, by itself, will give some indication of the success which has attended the efforts made to utilize the stores of atmospheric nitrogen; and chemists surely may justifiably feel some pride and satisfaction by reason of the fact that in the solution of the great problem of the fixation of atmospheric nitrogen, their ingenuity has not been found wanting.

---

[1] While the exact nature of the catalyst is kept secret, it may be regarded as oxide of iron to which potassium oxide, molybdenum, aluminium oxide or other substances are added to increase the efficiency.

[2] This carbon dioxide is produced in the process used for obtaining the hydrogen required for the synthesis of ammonia, namely, by passing water-gas and steam over a catalyst. Hydrogen and carbon dioxide are formed. When semi-water-gas is used a mixture of hydrogen, nitrogen and carbon dioxide is obtained.

In recent years the substance, *urea*, $CO(NH_2)_2$, first known as a product of animal metabolism, has begun to come into use as a fertilizer. It is produced industrially by the direct union of ammonia and carbon dioxide, under the influence of a catalyst, at a temperature of about 150° C. (302° F.), and under a pressure of about 70 atmospheres. The reaction is represented by the equation, $CO_2+2NH_3=CO(NH_2)_2+H_2O$.

Besides potassium, phosphorus and nitrogen, a number of other elements are required to act either as plant nutrients or to improve the fertility of the soil. Of these, perhaps the most important is calcium in the form chiefly of calcium carbonate (limestone, chalk) or of slaked lime (calcium hydroxide). The addition of lime to the soil is of importance, in the first place, in order to prevent undue acidity; but it has also a specific action not possessed, say, by magnesium. The fertility of a soil depends in great measure on the amount and nature of the colloidal material (*Chap.* 11) present; and the compounds of calcium are of great value in bringing about such a degree of flocculation and deflocculation of the colloids in the soil as to secure adequate aeration of the soil and the retention of the soluble salts.[1]

Magnesium, also, is an element which must be present in the soil, for it is an essential constituent of chlorophyll, the green colouring matter of leaves, etc. Usually there is an adequate supply of magnesium salts in the soil, but, if not, they must be added.

Whereas the elements already referred to are to be regarded as plant nutrients and must be present in the soil in adequate amount in a form which the plant can assimilate, investigation has shown that the health of a plant and the flavour of fruits and vegetables may depend on the presence in the soil of other elements in minute quantities. These *trace elements*, as they are called, seem in their action to partake somewhat of the character of catalysts, and to resemble the hormones (*Chap.* 16) in the animal organism. Small quantities of iron, for example, seem to facilitate the formation of chlorophyll, although chlorophyll itself contains no iron; and other elements—manganese, boron, copper, cobalt, zinc—although they may be harmful when present in large amount, have a beneficial action on the health of the plant when present in minute quantities.

---

[1] For improving the soil structure, especially of heavy clay-silt soils, chemists have produced various complex compounds known as *krilium*. Through the addition of this, in small amount, the soil becomes more porous, the water-holding capacity and aeration are increased, and there is a resulting improvement in root growth.

During the present century it has come to be realized that two elements especially, boron and manganese, are necessary for the health of higher plants, although the amounts required may be very small. Manganese seems to be an essential factor in plant metabolism and growth, and acts, apparently, as a catalyst of the enzymic reactions of the organism. Applications of manganese and zinc compounds to marshland fields in Kent, for example, increased the yield of potatoes from 7 to 11 tons per acre. Fruit trees, also, may have to be treated with a manganese salt to enable them to fruit.

Boron has been found to be essential for the normal growth of a number of plants, but the addition of 1 part of boric acid in 12,500,000 parts of water has been found sufficient to prevent signs of malnutrition. Various plant diseases, also, such as internal cork of apples, heart rot of sugar-beet and brown heart of swedes, have been found to be due to a boron deficiency and may be prevented by applications of borax (sodium borate) to the soil. Similarly, the disease known as mottle-leaf of citrus has been shown to be induced by a deficiency of available zinc in the soil.

Large tracts of worthless pumice country in North Island, New Zealand, have been brought into agricultural use by the addition not solely of superphosphate but also of the trace element cobalt; and, in South Australia, Ninety-mile Desert is being made to 'blossom as the rose' with the help of small amounts of zinc and copper sulphate, in addition to more abundant applications of superphosphate.

In S.E. Australia addition of a small amount of copper salt to the soil was found to be necessary for the growth of oats, wheat and lucerne; and copper is also necessary in pasture to put 'crimp' into sheep's wool. In South Australia, also, large areas of previously worthless land have, it is stated, been brought into agricultural use through the addition of only half an ounce per acre of molybdenum.

While chemists have rendered important service to agriculture by the production of an ample supply of fertilizers, they have also rendered a scarcely less notable, and perhaps more spectacular, service by providing the means for combating and controlling the chief enemies of food crops—weeds which deprive the soil of light, moisture and nutrient salts; and insects and fungi which attack and destroy the growing crops.

For many years farmers protected their crops of wheat and oats against the competition of charlock and other weeds by spraying their fields with sulphuric acid, a liquid somewhat unpleasant to handle. Now, however, chemists, through their study of plant hormones (*Chap.* 16), have succeeded in preparing growth-regulating substances which, in certain concentrations, act as selective weedkillers. They destroy preferentially plants belonging to the class of dicotyledons (to which most weeds belong) and leave unharmed grass, wheat, barley, etc., which belong to the class of monocotyledons. Millions of acres of food-growing land are now sprayed with the synthetic growth-regulating substances 'methoxone' (MCPA) and 2,4–D, which destroy charlock, corn buttercup, etc., without damaging the cereal crop. This is the chemist's modern solution of the farmer's age-long problem of the tares and wheat (Plate 19).

Synthetic growth regulators, also, are of value in promoting root formation in seedlings and cuttings of plants; in preventing or decreasing the premature drop of apples and pears; in bringing about the setting or formation of fruit (*e.g.* tomatoes) from sterile or unpollinated flowers; and in preventing the sprouting of stored potatoes.

Against insect pests chemists have prepared a number of insecticides (*Chap.* 13), which have proved effective in controlling the ravages of insects from the boll-weevil to the wireworm and from the Colorado beetle to the all-devouring locust;

and fungicides have been produced to combat mildew on vines and fruit trees, 'mouldy rot' of rubber trees, etc.

Although the fixation of atmospheric nitrogen has been considered only as a means of obtaining nitrogenous fertilizers, a brief reference to the industrial importance of nitrogen should not be omitted. Owing to the large amount of heat which becomes latent, and the consequent lowering of temperature which takes place, when liquid ammonia is converted into vapour, this substance is widely used at the present day in refrigeration. Ammonia is now also being used to an increasing extent for the production of *nitric acid*, which, as we have learned, is an essential reagent in the manufacture of explosives and is also required in the dye industry, as well as for the production of the oxides of nitrogen used in the manufacture of sulphuric acid by the lead chamber process. Previous to 1913, Chile saltpetre was the only practicable source of nitric acid,[1] and it is therefore clear that a country whose supplies of this salt might be cut off would, in time of war, be rendered powerless. It was, indeed, under the stimulus of the apprehension that such might be the fate of his country, that the German chemist, WILHELM OSTWALD, in the early years of this century, addressed himself to the successful development of a process of obtaining nitric acid from ammonia. Just as platinum acts as a catalyst for the combustion of hydrogen, so also it acts as a catalyst for the combustion of ammonia; and when a mixture of ammonia and air is passed over platinum, or platinum-rhodium alloy, in the form of wire gauze heated to a temperature of about 800° C. (say, 1470° F.), the ammonia reacts with the oxygen of the air to form oxides of nitrogen which, dissolved in water, yield nitric acid. By suitably regulating the process of oxidation, one can also obtain *ammonium nitrate*, NH_4NO_3, which is used as a fertilizer and as a constituent of high explosives.

The social-economic consequences of these developments in chemical industry have been stupendous. It was in 1913 (a noteworthy and ominous date) that Germany established the synthetic production of ammonia on an industrial scale; and since the later years of the war of 1914–18 she has obtained, through that process and through the catalytic oxidation of ammonia, all the ammonium nitrate and nitric acid which she has required for use in explosives and in the manufacture of explosives and nitrogenous fertilizers.

---

[1] Obtained by heating Chile saltpetre with sulphuric acid: $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$ (nitric acid).

Chapter 9

GLASS, SODA, SOAP, LIME AND CLAY

IN the previous chapter there was discussed one of the younger of the chemical industries, the production of synthetic ammonia, an industry which was developed at the call of necessity to contribute to the well-being of man and the advance of civilization. In the present chapter we shall turn our attention, in the first place, to one of the oldest industries, which, by reason of the unique and valuable properties of the product, is still one of the foremost industries of civilized countries, the industry of glass-making.

Many, doubtless, are familiar with the legend reported by the Roman writer Pliny in the first century of our era, which ascribed the discovery of glass to a party of Phœnician sailors who were forced by stress of weather to land on the sandy shore under Mount Carmel. Here, standing their cooking-pots on lumps of soda, with which their ship was laden, they observed the soda and the sand to fuse together under the heat of the fire, and so to form a glass. Although it may be that it was by some such accident that glass was discovered, and although the Phœnician towns of Tyre and Sidon were, at an early period, almost as celebrated for their glass as for the famous purple dye which coloured the robes of kings, it is to Egypt that one must look for the first knowledge of glass or glass-like material; to that country which, as Herodotus wrote, 'contains more wonders than any other land, and is pre-eminent above all countries of the world for works which almost baffle description.' The representation of the art of glass-blowing on the walls of the tomb of Tih (about 3800 B.C.), with which every visitor to Egypt is familiar, and the discovery of glass beads and ornaments among the ruins of the ancient city of Memphis, bear testimony to a knowledge of this material at a very early period in Egyptian civilization. What mankind owes to the first discoverer of the process of making glass, it is scarcely possible to describe. That first artificer in glass, as Dr. Johnson wrote, 'was facilitating and prolonging the enjoyment of light, enlarging the avenues of science, and conferring the highest and most lasting pleasures; he was enabling the student to contemplate nature and the beauty to behold herself.' And in modern times glass has undergone a wonderful evolution through the work and labours of chemists, who have shown how, by variation of the composition, the properties of glass may be altered in a most marvellous degree. Through the production of different kinds of glass there has been made possible the construction of apparatus for the most diverse uses, prisms and lenses for lighthouses, microscopes, telescopes, photographic cameras and other instruments, which have contributed to the service of man and a knowledge of the universe.

Before considering more fully the nature and properties of glass, however, there are one or two points of general importance to which it is necessary to direct attention.

Everyone is familiar with the statement that matter can exist in three states—solid, liquid and gaseous; and this statement is familiarly illustrated by the substance water, which is well known in the three forms of ice, water and steam. By elevation of the temperature, solid is made to pass into liquid, and liquid into gas, whereas by lowering the temperature the reverse series of changes is brought about.

At the present moment it is the change from solid to liquid, and more especially from liquid to solid, that claims our interest; and in using the term solid, I mean crystalline solid, and not amorphous solid. In a crystalline solid the particles are arranged in a definite geometrical form and give rise to a structure bounded by plane faces or surfaces, such as we see in the naturally occurring rock crystal, amethyst, etc.; whereas an amorphous solid does not naturally assume any definite shape, although it may, of course, be cut into definite forms in imitation of crystals. When a crystalline solid is heated it is found that it passes, *at a definite temperature*, known as its melting-point, from the solid to the liquid state, whereas an amorphous solid, like sealing-wax for example, gradually loses its rigidity and possesses, therefore, no definite melting-point.

When a crystalline solid substance is heated, it is found that melting or liquefaction occurs as soon as the melting-point is reached, and it has never yet been found possible to heat a crystalline solid to a temperature above its melting-point without such a change occurring. If, however, a liquid is cooled down, it is found quite generally that the temperature can be lowered below the normal freezing-point, or below the melting-point of the solid, without any of the solid form being produced. One can, for example, with care, cool water to a temperature much below 0° C. (32° F.) without any ice being formed, and liquids which are in this way cooled to below the normal freezing-point are said to be *supercooled*. Such supercooled liquids appear to be quite stable—they can, apparently, be kept for any length of time unchanged—provided that all traces of the solid form are rigidly excluded. If, however, even a minute trace, even the ten thousand millionth part of a grain, of the solid substance—a particle which might dance as a mote in the sunbeam—is brought into contact with the supercooled liquid, the state of apparent equilibrium is upset, separation of the crystalline solid form begins, and the process goes on until all the liquid has passed into solid.[1] The process of crystallization, however, does not take place at once throughout the whole mass of the liquid, but only those portions of liquid which are in contact with the solid crystallize out, and the rate at which crystallization proceeds depends also on the degree of supercooling. The further a liquid is cooled below the normal freezing-point, the faster will solidification occur once it has been started. This law, however, is subject to modification through the operation of another factor. It has already been pointed out that the speed with which a chemical change takes place depends on the temperature, the speed being all the greater the higher the temperature, and becoming less as the temperature is lowered. Similarly with the process of crystallization. When crystallization is started in a supercooled liquid, two opposing factors operate to influence the speed of crystallization. At first the effect of supercooling is predominant and so, as the degree of supercooling is increased, the rate of crystallization also increases; but after a point, the effect of the lowering of temperature counterbalances the effect of the supercooling, the rate of crystallization ceases to increase as the temperature is lowered, and in fact begins now to decrease. There is, therefore, a certain temperature, a certain degree of supercooling, at which the velocity of crystallization is a maximum, and below which it becomes less and less; and, ultimately, it becomes practically equal to zero. The supercooled liquid no longer crystallizes even when brought into contact with the crystalline solid.

---

[1] When the cooling is carried out slowly, it is found that substances differ greatly in the readiness with which they remain supercooled, but, in general, when a substance has been supercooled to a certain extent, crystallization or separation of the solid in the crystalline form takes place spontaneously, that is, without the previous addition of the solid form.

We know, however, that as a liquid is cooled down, it becomes more and more viscous, and at last it becomes so vicious that it does not 'run' at all so far as ordinary observation can detect, and so we call it a solid. An *amorphous* solid is just such a supercooled liquid, a liquid cooled so far below its crystallization point that the rate of crystallization is infinitely slow. In this way are formed, for example, the glassy lavas, or obsidians, by the rapid cooling of molten lava, as well as ordinary glass with which we are so familiar.

When a supercooled liquid or 'glass' is maintained at a temperature in the neighbourhood of the softening point, spontaneous crystallization may set in, and thereby cause the glass to lose its transparent, vitreous character; the glass, it is said, *devitrifies*. Under certain circumstances, this may prove a source of much annoyance.

SILICA AND GLASS

A substance which affords an excellent illustration of the behaviour which has just been discussed is quartz or silica (an oxide of the element silicon), a substance which is very familiar to everyone. It occurs as the clear, glassy particles which form sea-sand, and which can also be readily distinguished in granite; coloured by certain impurities it forms the well-known ornamental stones, the cairngorm and the amethyst, while in the pure colourless form it is known as rock crystal, which ordinarily crystallizes in six-sided prisms ending in six-sided pyramids. Silica occurs, also, in the amorphous state, as agate, flint, etc., and in a hydrated form as opal. The waters of the Icelandic geysers, as well as those of the Yellowstone Park, U.S.A., contain silica in solution, and this is deposited as a compact mass around the mouth of the geyser (Plate 20).

When crystalline quartz is heated in the oxyhydrogen blowpipe flame, or in a specially constructed electric furnace, to a temperature of about 1650° C. (3000° F.), it melts to a colourless liquid;

and when this liquid is cooled fairly rapidly, the quartz can be obtained as a clear, colourless, glassy mass—a supercooled liquid—which looks just like ordinary glass, but is much more transparent. It is, in fact, the most transparent solid material known. This fused quartz, or quartz glass, possesses the exceedingly valuable property that it expands and contracts only very slightly with alteration of the temperature (its coefficient of expansion is less than one-tenth that of glass), and for this reason it can, unlike ordinary glass, be rapidly heated or rapidly cooled without cracking. It can, for example, be heated red hot and then plunged into cold water, or when cold it can be suddenly introduced into the blowpipe flame; or a wire enclosed within a tube of quartz glass may be heated to a bright red heat by means of an electric current while the tube is immersed in cold water, and the quartz glass remains, in all cases, uncracked. By reason of this property, quartz glass, formed into apparatus of various kinds, has come increasingly into use, more especially in cases where rapid changes of temperature are encountered. Although readily attacked by alkalis, it is very resistant to acids, except hydrofluoric acid. Apart from its scientific and industrial uses, fused silica is now largely used in the manufacture of globes for incandescent gas burners and in electric radiators.

When heated for some time to a temperature of about 1150° C. (say, 2100° F.), a temperature considerably below the point at which it becomes fluid, the glassy quartz passes into crystalline form; it 'devitrifies,' and can then no longer withstand, as before, sudden changes of temperature.

Unlike fused quartz or silica glass, ordinary glass is not a single substance but a homogeneous mixture of substances. When quartz or silica, which occurs in great abundance as sea-sand, is heated together with soda (sodium carbonate), the silica, being an acid oxide, displaces the carbonic acid from the carbonate and a compound is obtained known as sodium silicate. When this is allowed to cool, it solidifies to a glassy material known as *water-glass*, so called because of its solubility in water. Commercial water-glass is an aqueous solution of sodium silicate with excess of silica dissolved in it, and is used as an adhesive for glass and porcelain, as a preservative for eggs and for numerous other purposes. Its use depends on the fact that it readily forms a gelatinous film on objects. If, instead of heating sand or quartz with soda (or potash) only, one also adds other metal oxides or carbonates, such as lime, or alumina (oxide of aluminium), or oxide of lead, mixtures of silicates are obtained which solidify to glasses that do not dissolve in water, and which constitute what one ordinarily calls glass. Glass has, therefore, no definite composition, and by varying not only the constituents but also their relative amounts, glasses of various kinds and possessing very different properties can be produced. Glass for table-ware and for general use consists essentially of a mixture of the silicates of sodium and of calcium, but potassium and aluminium silicates are also generally present. The quality and appearance of the glass depend largely on the purity of the materials employed in its manufacture.

Silica, in the form of a fine white sand,[1] is mixed thoroughly with selected amounts of sodium carbonate and sulphate,[2] potassium carbonate, calcium carbonate (in the form of pure white chalk or limestone), and felspar (to supply the aluminium). The mixture is melted in large fire-clay pots or in tanks, heated generally by means of gas.[3] At first the molten mass is almost opaque owing to the multitude of bubbles of carbon dioxide which permeate it, but these bubbles gradually escape, and a clear liquid is obtained. The desired articles can then be formed either by pouring the molten glass into moulds or by blowing. In the latter case, a quantity of molten glass is taken up on the end of a long metal tube, and by blowing through the tube, hollow articles of varied shape can, by the expert skill of the glassblower, be obtained.

The blowing of electric light bulbs and of bottles, and the production of sheet glass for glazing, etc., are now carried out in automatic or semi-automatic machines; and the introduction of these machines has made necessary various alterations in the composition of the glass mixture. For the successful working of these machines the molten glass must set or solidify more slowly than the glasses worked by hand. This could be secured by reducing the amount of calcium oxide and increasing the amount of soda, but the resulting glass would then be too readily corroded by water. If, however, a small amount of magnesia and alumina is added to the glass mixture, a sufficiently slow setting glass can be obtained which can be worked in the machine without showing devitrification and which is not corroded on exposure to the air. Such a glass has the percentage composition: SiO_2, 72·5; Na_2O, 13·5; CaO, 10·5; MgO, 2·0; Al_2O_3, 1·0.

---

[1] An abundant deposit of sand at Lochaline on the Sound of Mull, in Scotland, has been developed for glass manufacture. Its purity exceeds that of the best continental quartz sand imported before 1940 from Belgium, Holland and France.

[2] The addition of sodium sulphate has the effect of strengthening the finished glass.

[3] A process for the melting of glass by means of an electric current has recently been introduced.

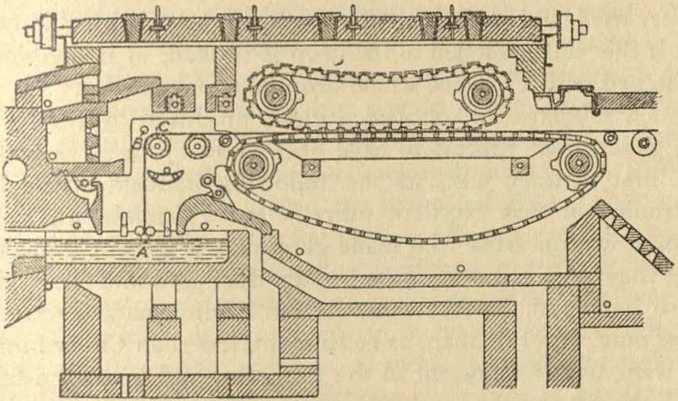


FIG. 16.—PRODUCTION OF SHEET GLASS BY THE LIBBEY-OWENS PROCESS

The sheet of glass which is drawn from the tank of molten glass at point A, passes over the rollers at BC and then passes between moving endless bands.

In the production of sheet glass by the Libbey-Owens process, a metal bar is lowered into the molten glass which is caused to well-up through a slit in a fireclay plate. As the bar is raised, the glass adheres to it and solidifies, and in this way a sheet of glass is formed. This sheet, after rising out of the tank of molten glass, passes over a roller and is drawn along in a horizontal position (Fig. 16).

The surface of sheet glass is not quite plane, but is covered with slight depressions and ridges, and in consequence of this, objects viewed through such glass are more or less distorted. To get rid of this defect, the sheet glass is ground and polished, as in the case of plate glass, and in this way one obtains what is known as 'patent plate.' Such glass is largely used for the framing of pictures.

Glass articles which have been formed by blowing or moulding must be reheated to near the softening point and then placed in an 'annealing' chamber where they can cool very slowly. The purpose of this is to get rid of the stresses which are set up in the rapidly cooled glass and which render the glass very liable to fall to pieces when scratched. This behaviour can be illustrated by what are known as Rupert's drops,[1] obtained by dropping molten glass into hot oil, so that the glass is suddenly cooled. This glass is very hard, and can withstand even heavy blows with a hammer, but if the 'tail' attached to the drop is broken, or if the glass is scratched with a file, the whole drop falls to a powder.

Such hardened or toughened glass, produced by cooling the hot glass in oil, appears to have been known at least as early as the first century A.D., as the following incident, related by Petronius in that excellent satire, *Cena Trimalchionis*, shows: 'There was an artist who made glass vessels so tough and hard that they were no more to be broken than gold and silver ones: It so happen'd that the same person having made a very fine glass mug, fit for no man, as he thought, less than Cæsar himself, he went with his present to the Emperor, and had admittance; both the gift and the hand of the workman were commended, and the design of the giver accepted. This artist, that he might turn the admiration of the beholders into astonishment, and work himself the more into the Emperor's favour, begged the glass out of Cæsar's hand; and having received it, threw it with such a force against a paved floor, that the most solid and most firmest metal could not but have received some hurt thereby. Cæsar also was equally amazed and troubled at the action; but the other took up the mug from the ground, not broken but only a little bulg'd, as if the substance of metal had put on the likeness of glass; and therewith taking a hammer out of his pocket he hammer'd it as if it had been a brass kettle, and beat out the bruise: and now the fellow thought himself in heaven, in having, as he fancied, gotten the acquaintance of Cæsar, and the admiration of all mankind; but it fell out quite contrary to his expectation: Cæsar asking him if anyone knew how to make this malleable glass but himself, and he answering in the negative, the Emperor commanded his head to be struck off; "For," said he, "if this art were once known, gold and silver will be of no more esteem than dirt."' In such fashion did the Emperor Tiberius encourage and foster science.

---

[1] So called because introduced as a toy by Prince Rupert in the seventeenth century.

To obviate the danger of personal hurt by sharp splinters of glass, it is required by law that the windscreens of motor cars shall be made of safety glass. Such safety glass was first produced, under the name of 'Triplex Glass,' by pressing together, in a hydraulic press heated by hot water, two sheets of plate glass with a sheet of transparent plastic material between. When such glass is struck a blow sufficiently hard to shatter it, the broken pieces of glass, often dangerously large and with sharp points or edges, do not fly but remain firmly adhering to the plastic inter-layer. Still more recently, 'Armourplate' glass, or 'Triplex Toughened' glass, has been introduced, and, in Great Britain, has largely displaced the laminated glass. This is not, in spite of its name, a triplex glass at all, but a single sheet of plate glass which is toughened or hardened, like Rupert's drops, by being heated to the softening-point and then cooled rapidly, but in a carefully regulated manner, by blasts of cold air. By this treatment the glass acquires a much greater strength and flexibility, and a greater resistance not only to breakage by bending but also to fracture by impact. Thus, while untreated plate glass, one-quarter of an inch in thickness, was fractured by a weight of 1·68 lb. falling from a height of 12·7 inches, the toughened 'Armourplate' glass was broken only when the same weight was dropped from a height of 122 inches. Moreover, when this toughened glass is broken it does not splinter into dangerously large and sharp pieces which may inflict severe or even fatal wounds, as does ordinary plate glass, but breaks up into a mass of small and comparatively harmless fragments. Since 'Armourplate' glass cannot be cut or chipped without falling to pieces, the plate glass must be cut to shape before being subjected to the hardening process (Plates 21 and 22).

A reinforced glass, much used for constructional purposes (*e.g.* roofing), can be obtained by embedding in the still molten glass a network of steel or nickel-steel wire.

By a systematic study of the influence of a large number of substances on the properties of glass, hundreds of different glasses have been produced and their physical and optical properties examined. Some of these special glasses have proved themselves to be of the highest value and have made possible the construction of apparatus by which scientific knowledge and material well-being have been greatly promoted.

Heat-resisting glass with a low coefficient of expansion is now widely used for cooking utensils (*e.g.* pyrex ware). Such glass is obtained by reducing the proportion of soda and increasing the proportion of silica; and boric oxide, which greatly reduces the coefficient of expansion of glass, is also added. Thus, pyrex glass contains about 80 per cent. of silica, 12 per cent. of boric oxide, and smaller amounts (3-4 per cent.) of soda and alumina (aluminium oxide). The value of glass as compared with metalware for cooking purposes depends on the fact that glass reflects a comparatively very small proportion of the radiant heat which reaches it, so that baking takes place more rapidly in glass than in metal dishes.

To avoid distortion with change of temperature, a glass of the pyrex type, with low coefficient of expansion, was adopted for the reflector of a large 200-inch telescope constructed for the observatory at Pasadena, California. The surface of the glass was coated with a layer of aluminium by the method of vaporization in a high vacuum (p. 88).

By fusing silica with a mixture of potash and red lead (oxide of lead, Pb_3O_4), a lustrous glass with a high refractivity is obtained, and is known as 'crystal.' When cast in suitable moulds, or, preferably, cut with a wheel and polished, it is much prized for vases and ornamental dishes of different kinds. A still more lustrous glass can be obtained by replacing part of the silica in the crystal glass mixture by boric acid, and so giving rise to what is called generally a boro-silicate glass. By reason of its brilliant lustre and high refractive power, such a glass, when suitably cut, sparkles and flashes in a myriad colours. It is, therefore, largely employed, under the name of 'strass' or 'paste,' for counterfeiting diamonds and, when suitably coloured, other gems as well.

The production of coloured or stained glass is easily effected by adding small quantities of suitable substances to the molten mixture of silicates. Thus, addition of iron oxide imparts a blue colour to the glass, whereas the addition of manganese oxide colours the glass an amethyst or purple shade. Salts of the metal uranium give to glass a yellowish green fluorescence, and are much used in the production of fancy glass. With cobalt oxide the colour is deep blue, while with gold, a ruby red is obtained. Paste coloured blue with cobalt, or red with gold, is used to counterfeit the sapphire and the ruby. These counterfeit gems must not be confused with the artificially prepared sapphires and rubies to which reference has already been made (p. 68). They can readily be distinguished from the latter or from the naturally occurring gems by their much greater softness.

In most cases the colour in glass is due to the formation of coloured silicates, silicate of manganese, silicate of cobalt, etc.; but in the case of ruby glass, the colour is due to the presence of gold in what is called the *colloidal state* (*Chap.* 11). That is, the gold is present in particles so minute that they are invisible even under a powerful microscope. If, however, too much gold is added, the metal may separate out in visible particles and so render the glass opaque. If one adds selenium to a glass in which the place of lime has been taken by zinc oxide, a highly transparent red glass, much used for signal lamps, tail-lights of automobiles, etc., is obtained. As in the case of gold, the selenium is present in the colloidal state.

The transparency of glass, not only for the rays of visible light but also for the invisible rays of longer wave-length (infrared) and of shorter wave-length (ultraviolet), can be greatly increased by the use of very highly purified materials. On the other hand, glass containing a considerable proportion of iron, in what is known as the ferrous state,[1] is used for making goggles to protect the eyes from infrared rays (heat rays) and ultraviolet rays.

Glasses can also be obtained which are opaque to visible radiations but transparent to ultraviolet rays (*e.g.* Wood's glass, which contains nickel oxide), or to infrared rays. Glass opaque to visible light but transparent to infrared rays is used in signalling and in the construction of burglar alarms.

---

[1] Iron forms two oxides, FeO and Fe_2O_3, known respectively as ferrous oxide and ferric oxide. From these oxides are derived two series of salts, ferrous salts and ferric salts. Ferrous oxide gives a blue, ferric oxide a brown colour to glass.

Glass is used in large quantities for the production of mirrors, which are greatly superior to the polished metal mirrors used by our forefathers and sometimes also at the present day. In order to avoid distortion, plate glass, the surface of which has been polished quite plane and smooth, must be used, and one side of this is 'silvered.' Formerly, this was effected by coating the glass with an amalgam of tin and mercury, but mercury is a very expensive metal and its use also involves the danger to the workman of mercurial poisoning. For the production of mirrors, therefore, mercury has been superseded by silver, the use of which is not only free from danger, but allows also of a whiter reflecting surface being obtained. By adding caustic soda and ammonia to the solution of a silver salt, *e.g.* silver nitrate, a solution is obtained from which metallic silver can readily be caused to separate out by the addition of certain substances, such as glucose. This solution is poured over the well-cleaned surface of the mirror glass resting on a heated table. Silver separates out very slowly and forms a coherent and highly reflecting coating on the surface of the glass. Aluminium, deposited on glass, is now also being used in place of silver for the production of mirrors.

Glass wool or 'Fibreglass,' produced by drawing molten glass, issuing from fine nozzles, into filaments, and by other processes, is widely used as an insulating material for electricity, heat and sound; as a reinforcing material for plastics; for the production of fire-proof fabrics, and for other purposes (Plate 23).

SODA

The use of sodium carbonate or soda in the manufacture of glass brings that industry into the closest relations with an important series of chemical industries, namely, the manufacture not only of soda itself but also of sulphuric acid, hydrochloric acid, chlorine and bleaching powder.

Sodium carbonate has been known from remotest ages as forming a deposit on the floor and shores of the soda-lakes of Egypt, and this was probably the chief source from which the early Phœnician traders obtained the salt. At the present day, these natural deposits are again being worked (*e.g.* at Lake Magadi in East Africa, and at Owens Lake, California). Formerly, soda was called 'nitre,' and by this name it is referred to in the Bible.[1]

Previous to the nineteenth century, the sodium carbonate required, more especially, for the manufacture of glass and of soap, to which we shall refer presently, was obtained mainly from the ash of the saltwort (*Salsola kali* L.). This was grown on large areas reclaimed from the sea along the coast of Spain, and more especially along the coast of Alicante, and was reduced to ash by burning. This ash, containing up to 15–20 per cent. of sodium carbonate, was sold under the name of *barilla*.[2] The supply, however, was scanty, and barely sufficient to meet the demand. There was, therefore, great need for an abundant source of cheap soda, and the Academy of Paris offered a prize for a process of converting common salt, or sodium chloride, of which there are such abundant supplies occurring naturally, into sodium carbonate or soda. This problem was solved by the French chemist, NICOLAS LEBLANC, and in 1791 a factory for the manufacture of soda by the Leblanc process was established at St. Denis. In 1793, however, this was confiscated by the Committee of Public Safety, and in 1806, filled with despair, the inventor of a process which has contributed so much to the comfort and well-being of men by giving to them cheap glass and cheap soap, ended his days by his own hand.

Important and successful as was the Leblanc process during the first half and more of the nineteenth century, it had by the end of the century practically succumbed before an economically more successful rival, the so-called ammonia-soda or Solvay process. The reaction underlying this process, a reaction between sodium chloride and ammonium bicarbonate giving rise to sodium bicarbonate and ammonium chloride, had been placed before the French Academy in competition with the Leblanc process; but the Academy, fearing the loss of ammonia, rejected the process in favour of that proposed by Leblanc. In 1838,

---

[1] 'As he that taketh away a garment in cold weather, and as vinegar upon nitre, so is he that singeth songs to an heavy heart' (Proverbs xxv. 20). Soda, when acted on by vinegar (acetic acid), is decomposed with brisk effervescence due to the production of carbon dioxide.

[2] The barilla industry was introduced into Spain by the Saracens, who called the saltwort, or the ash of saltwort, *al qali* or *al kali*. From this the term alkali is derived. On the salt steppes of the Argentine the saltwort is still grown, and burned for the production of soda.

DYAR and HEMMING, in England, took out a patent for the working of the ammonia-soda process, but production on an industrial scale was unsuccessful. In 1863, however, after many others had failed, the Belgian chemist, ERNEST SOLVAY, successfully developed the process whereby soda can be produced more economically and in a purer form than by the method of Leblanc. The process depends on the fact that when carbon dioxide is passed into a solution of common salt saturated with ammonia, sodium bicarbonate (*baking soda*) is deposited. By heating the bicarbonate, $NaHCO_3$, carbon dioxide and water are driven off and sodium carbonate, Na_2CO_3, is obtained.[1] When this is crystallized from water it forms clear, colourless crystals, $Na_2CO_3, 10H_2O$, known as *washing soda*. *Bath salts* consist, as a rule, of sodium carbonate, mixed with borax or other salts, tinted and perfumed. *Baking powders* contain sodium bicarbonate and a solid organic acid, such as citric or tartaric acid or cream of tartar. So long as this mixture is kept dry, no action occurs; but when it is brought in contact with water, as in the preparation of dough, the acid reacts with the bicarbonate and carbon dioxide is evolved. The dough is thereby caused to rise.

Although the Leblanc process is no longer used for the manufacture of soda, the first stage of the process, which consists in heating sodium chloride (common salt) with sulphuric acid, is still carried out for the production of hydrochloric acid (muriatic acid or spirit of salt) and of sodium sulphate. In this reaction, a knowledge of which goes back to before the seventeenth century, the sodium chloride is converted into sodium sulphate or 'salt-cake,' which is used in the manufacture of glass, and at the same time large quantities of *hydrogen chloride* or hydrochloric acid gas, HCl, are produced. When this gas is passed into water, in which it is exceedingly soluble, the acid, *hydrochloric acid*, is obtained. This is one of the most important of the so-called mineral acids.

Hydrogen chloride, moreover, is a source of the very important substance, *chlorine*; for, when hydrogen chloride mixed with air is passed over heated pumice, impregnated with copper chloride, the copper chloride acts as a catalyst and accelerates the oxidation of the hydrogen chloride by the oxygen of the air, with formation of water and of chlorine—a process known as *Deacon's process*.

---

[1] According to the equation: $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$.

Chlorine is now produced mainly by an electrolytic process (p. 176).

CHLORINE is a gaseous element with a characteristic, choking smell, and when inhaled is very destructive of the tissues of throat and lungs. It is a most valuable bleaching and disinfecting agent and is also extensively employed in chemical industry for the production of dyes, insecticides, cleaning agents, etc. Its use for the sterilization of the water supply of towns, as well as for the sterilization of the water of swimming pools, is well known.

For convenience of transport and use, chlorine may be passed over slaked lime, which reacts with it and gives rise to *bleaching powder*, or chloride of lime as it is popularly called. For this bleaching powder, invented by CHARLES MACINTOSH and first produced in 1799 by CHARLES TENNANT in Glasgow, a great demand sprang up early last century, due to the development not only of the textile (cotton and linen) but also of the paper industry, the raw materials for which require to be bleached before use. Nowadays, bleaching powder is used on a considerably reduced scale and chlorine is transported mainly in the liquid form in steel cylinders.

SOAP

Another very large industry which is dependent on the use of soda is that of soap-making. Even at an early period, about the beginning of the Christian era, a material resembling what is now known as soft soap, and used largely as an ointment, was prepared by boiling fat with potashes; and although in later times the manufacture of soap developed considerably, it was not till early last century that it passed from being a handicraft carried on by rule of thumb, to an industry increasingly controlled by a more exact knowledge of the properties of the materials used.

It has already been pointed out that the animal and vegetable fats and oils were shown by the French chemist, Chevreul, to be compounds of glycerine with different acids which could be obtained by boiling the fats and oils with dilute sulphuric acid, or by treating them with superheated steam. This process of *hydrolysis*, as it is called, or decomposition by water, which is catalytically accelerated by acids, can also be facilitated by caustic soda (sodium hydroxide), or caustic potash (potassium hydroxide), and the acid of the fat or oil then combines with the soda or the potash to form a sodium or potassium salt of the acid. This sodium or potassium salt of the fat or oil acid constitutes soap; and hence the process of decomposing a fat or oil by means of alkali is known as *saponification*.

Caustic soda (NaOH) and caustic potash (KOH) are obtained by boiling solutions of sodium carbonate or potassium carbonate with slaked lime or calcium hydroxide, $Ca(OH)_2$. Mutual decomposition takes place with formation of sodium or potassium hydroxide and calcium carbonate, and the latter, being insoluble, separates out. Nowadays an electrolytic process (p. 176) in which not only caustic soda or caustic potash is formed, but also chlorine and hydrogen, is assuming ever greater proportions, and may one day supersede the method which has just been described.

Although soap can be obtained by using either caustic soda or caustic potash, the nature of the product obtained in the two cases is different, the potash soaps being soft, the soda soaps hard.

The fats and oils used in soap-making are very varied in character. Formerly, animal tallow and olive oil were the chief raw materials employed, but, as has already been pointed out, the increased demand for margarine and other butter substitutes has driven the soap-maker to seek other sources of supply, and a number of different animal and vegetable oils have now been forced into his service. These are either used as such, for the manufacture of soft soap, or are first 'hardened' by the catalytic process referred to previously, for use in the manufacture of hard soap. By the admixture of different raw materials in varying proportions, soaps of different kinds and qualities can be obtained; and in the proper blending of the raw materials lies the art of the soap-maker, an art which is now guided by careful scientific investigation.

In the manufacture of soft soap or potash soap, different animal or vegetable oils, *e.g.* linseed oil, cotton-seed oil, soya-bean oil, are boiled with caustic potash. The oils are thereby decomposed with formation of glycerine and the oil acid, which combines with the potash to form soap. A thick paste is thus obtained which, owing to the presence of glycerine derived from the oil, does not dry up. Additions of water-glass and other 'loading' materials are frequently made.

In the manufacture of hard soaps or soda soaps, the melted fat is heated with a solution of caustic soda, the process of saponification being allowed to take place either in large pans or as the mixture flows continuously through a partitioned vessel. When saponification has taken place common salt is added, and this causes a paste of soap to separate out on the surface of the liquid, which contains not only the added salt and excess of alkali and various impurities but also the glycerine of the fat. Although, at one time, this liquid used to be run to waste, it is now subjected to a process of distillation in special vacuum stills in order to recover the *glycerine* (Plate 24).

The soap, after being boiled up with water to remove impurities and again 'salted out,' is hardened by cooling on steel rollers. From these it is scraped off in thin shreds which are kneaded together, mixed with colouring matter or perfumes, and extruded, under pressure, in the form of bars. The bars are then cut into lengths and moulded into tablets (Plates 25 and 26).

Not infrequently this 'genuine soap' is 'filled' by the addition of other substances, such as sodium carbonate and water-glass. The soap is thereby hardened, and since the added salts act as water-softeners, its detergent power is increased.

The familiar transparent soaps are obtained by dissolving pure soap in alcohol and then evaporating off the alcohol.

Almost endless is the list of modern commercial soaps now offered for sale for special purposes, in which, with the genuine soap, there are incorporated disinfectants, medicaments of various kinds, scouring materials such as infusorial earth, bleaching materials such as perborates, etc.

GLYCERINE, formed as we have seen as a by-product in the manufacture of soap, is a valuable substance, sometimes more valuable than the soap itself. It finds extensive use not only in the manufacture of dynamite and other explosives, but also in the production of synthetic resins known as 'Glyptals' (*e.g.* glyceryl phthalate). It is also used as a humidifying agent in rayon, cellophane and other industries, and as an 'anti-freeze' in the radiators of motor cars and in gas meters.[1]

Although obtained mainly by the hydrolysis or saponification of fats and vegetable oils, glycerine is now also produced on a large scale, more especially in the United States, from propylene, $CH_2:CH\cdot CH_3$, one of the gases formed in the cracking of mineral oils. It can also be produced by fermentation (*Chap.* 15). By the increased development of these processes, fats can be conserved for human consumption.

---

[1] The place of glycerine as an anti-freeze additive to water in the radiators of motor cars is now taken mainly by methanol or by glycol.

The cleansing power of soap depends on its physical as well as on its chemical properties; and in this connection its most important property is that it lowers the *surface tension* of water. What do we mean by this? Everyone knows that when water is brushed over a greasy surface, it does not form a continuous film wetting the surface, but breaks up into a number of separate drops, for all the world as if each little drop were surrounded by a thin elastic skin; and the force which keeps the water in the form of a drop is called the surface tension. It is to the action of surface tension that is due the proverbial ease with which water runs off a duck's back. If the surface tension is reduced sufficiently, if, as it were, one reduces the strength of the imaginary elastic skin surrounding the drop, then the water will spread out over the greasy surface and wet it; and this lowering of the surface tension can be effected by dissolving soap in the water.[1] This property of soap of lowering the surface tension of water is an important factor in its cleansing power, because it enables the water to wet and so to come into close contact with even a greasy surface. But there is another property of soap solutions which plays perhaps the most important part of all in the cleansing process. This is the property of emulsifying oils and fats. On shaking up any oil (olive oil, paraffin oil, etc.) vigorously with water, it is found that a milky liquid is obtained owing to the oil being broken up into a large number of droplets. But this milky appearance is not permanent; in the course of a few minutes the droplets of oil run together to form larger drops, which then collect as a separate layer on the surface of the water. The milkiness thus disappears. If, however, the oil is shaken not with pure water but with water containing a little soap, the droplets into which the oil breaks up are much smaller (the emulsion appearing, in consequence, much whiter than before), and they do not run together and form a separate layer on standing. The oil is permanently emulsified. And this is what happens when soap is used in cleansing a greasy surface to which dust and other dirt so readily adhere; the film of grease is broken up owing to the emulsifying action of the soap solution, and the grease and dirt are then readily washed away. The removal of dirt is also facilitated in a purely mechanical way by the lather or foam which the soap-water forms, the production of lather being another result of the lowering of the surface tension of water.

---

[1] The effect described here will be familiar to everyone who has interested himself in water-colour painting. To make the water-colour 'take,' a little ox-gall is added, when necessary, in order to reduce the surface tension of the water.

In the light of the explanation, just given, of the cleansing power of soap, attempts were made, especially in Germany owing to a shortage of fats during World War I, to produce other detergents very different in chemical nature from an ordinary soap or salt of a fat acid. Thus, by the action of sulphuric acid on higher unsaturated hydrocarbons of the ethylene type (p. 53), containing between ten and eighteen carbon atoms, acids are formed; and the sodium salts of these are found greatly to reduce the surface tension of water and to have valuable wetting and detergent properties.[1] Some of them, *e.g.* sodium lauryl sulphate, find use in shampoo powders. Since these substances do not form insoluble compounds with lime or magnesia, they can be advantageously used, even with hard water.

Synthetic wetting agents and detergents of varied chemical nature and with properties which make them specially suitable for specific purposes, are now being produced in very large amounts. They find extensive use, in home and factory, not only as detergent substitutes for soap but also as wetting agents to secure evenness of colour in dyeing; to increase the effectiveness of insecticide sprays; for degreasing metals and china ware, and for many other purposes.[2]

Although the salts of the fat acids with sodium and potassium, the ordinary soaps, are soluble in water, the salts with calcium and magnesium are insoluble. Consequently, when soap is brought into water containing salts of calcium or magnesium in solution, the soap is decomposed with production of the insoluble calcium or magnesium salt of the fat acid, which separates out as a scum. Thus—

---

[1] Substances which lower the surface tension of water are commonly spoken of as surface-active substances.

[2] Through the introduction of soapless detergents, larger supplies of edible fats and oils become available for human consumption.

Soluble soap (sodium stearate, etc.) and Calcium bicarbonate (sulphate, etc.)	give	Sodium bicarbonate (sulphate, etc.) and Insoluble soap (calcium stearate, etc.).

From its 'feel' in washing, water containing calcium or magnesium salts is called 'hard,' and, since the soap is decomposed, no lather can be obtained until sufficient soap has been added to combine with all the calcium and magnesium salts present. Moreover, since the bicarbonate or other salt of sodium which is formed does not lower the surface tension of water and has no power of emulsifying oils, the soap cannot exercise its proper cleansing function until after the removal of the calcium and magnesium salts.

Not only is hard water most wasteful of soap, but it may also be a source of annoyance, both domestic and industrial, owing to the separation out, in hot-water and steam boilers, of the salts of calcium and magnesium (the so-called 'fur'), which insulates the kettle or boiler and so causes a loss of heat. Explosions, moreover, may be caused in boiler tubes owing to the 'scale' cracking and so allowing water to come in contact with the overheated tubes. It is of importance, therefore, to get rid of or to reduce the hardness.

The formation of 'fur' or 'scale' may be prevented not only by softening the water, as explained in the following paragraphs, but also by the addition to the water of a small quantity of sodium hexametaphosphate $(NaPO_3)_6$, obtained by fusing the ordinary sodium phosphate, NaH_2PO_4. This hexametaphosphate is produced commercially under the trade name of 'Calgon' and prevents the formation of 'fur' by forming with the calcium salts soluble complex phosphates.

When the hardness of water is due to the presence of calcium bicarbonate (formed by the action on limestone, or calcium carbonate, of the carbon dioxide dissolved in rain water),[1] it can

---

[1] $$\underset{\text{Calcium carbonate}}{CaCO_3} + H_2O + CO_2 = \underset{\text{Calcium bicarbonate.}}{Ca(HCO_3)_2}$$

When calcium bicarbonate is heated, it decomposes into calcium carbonate, water and carbon dioxide.

be got rid of by boiling, and is therefore known as *temporary hardness*. On a large scale, the 'softening' of the water can be effected by the addition of slaked lime in proper amount (Clark's process). The soluble bicarbonate is thereby converted into the carbonate which, being insoluble, separates out and is removed by filtration: $Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$.

Hardness which is due to the presence of sulphate of calcium or magnesium cannot be removed by boiling, and is known as *permanent hardness*. It can be got rid of by the addition of sodium carbonate, or 'washing soda,' the calcium or magnesium being thereby thrown out of solution as insoluble carbonate. Hence the use of washing soda in the laundry.

For industrial and domestic purposes, another process for softening hard water has been introduced, known as the *permutit* process. Permutit[1] is an artificially prepared *zeolite*, sodium aluminium silicate, formed by fusing together quartz, alumina and sodium carbonate. When hard water is filtered through a layer of this material, the calcium and magnesium replace the sodium in the silicate, forming calcium or magnesium aluminium silicate, and are thus removed from the solution. The water is thereby rendered soft. When all the sodium has been replaced, the permutit ceases to be effective, but its activity can be restored by flushing with a solution of common salt (sodium chloride). By this means the sodium aluminium silicate is regenerated.

More recently, great advances in water purification have been made owing to the discovery, in 1935, by chemists working in the National Chemical Laboratory at Teddington, that certain synthetic resins and other products can remove from solution not only calcium and magnesium, but also sodium and other metals (*cations*), present in salts, while synthetic resins of another type can remove the acid ions (*anions*), such as sulphate and chloride (p. 170). Thus, by passing water containing, say, calcium, magnesium and sodium salts in solution through resins of the first type, the metal ions are removed and replaced by hydrogen ions, and the effluent contains only free acids. On passing this acid water through resins of the second type, the acids present are removed and replaced by carbonic acid. Water free from dissolved salts is thereby obtained. By passing a current of air through this water, the carbon dioxide (CO_2) is removed and the water then resembles distilled water in purity.

---

[1] *Permutit* is a trade mark for a number of different materials.

The activity of the resins can be restored by treatment with dilute sulphuric acid, in the former case, and with a solution of sodium carbonate, in the latter. By means of these ion-exchange resins, as they are called, industries can now obtain, much more cheaply than by distillation, water equal in purity to distilled water, or, also, water containing any concentration of salts that may be desired (*e.g.* for use as a potable water).

The methods just described for removing dissolved salts from water found, during the war, an application of the highest importance. Provided with suitable 'desalting' kits, airmen compelled to bale out over the sea were able to obtain a potable water from sea-water.

LIME

The solvent action on limestone of water containing carbon dioxide in solution, to which reference has been made, is of great economic and geological importance. Not only is the process mainly responsible for the production of hard water, which is met with in all limestone and chalk districts, but it is the chief agent by which lime is transported through the soil and rendered available for plants.

How great may be the effect of this solvent action of carbonic acid, acting through the ages, is seen from the great limestone caves, like the Mammoth Cave, Kentucky, which have been gradually eaten out of the solid rock by water containing carbonic acid in solution. No sooner, however, are these caves formed than Nature begins to fill them up again, for the rain-water, bearing carbonic acid in solution, percolates through the rock and dissolves it. On reaching the roof of the cave the water evaporates and leaves behind a minute grain of limestone; and as drop follows drop through endless years, grain is added to grain and an icicle-like *stalactite* hangs pendent from the roof. As Shelley has so beautifully written:

> From the curved roof the mountain's frozen tears,
> Like snow or silver or long diamond spires,
> Hang downward, raining forth a doubtful light.

If the drops of water come faster, some may fall to the floor of the cave and, evaporating there, build up a mighty column or *stalagmite*. Many and varied, graceful and grotesque, delicate and massive, are the forms which may thus be produced, and the sight presented by such a cave, suitably illuminated, is one of the most impressive that can be experienced.

Spring water carrying calcium bicarbonate in solution will deposit calcium carbonate as the carbon dioxide escapes and the water evaprates. In this way were formed the great terraced basins of limestone at Mammoth Hot Springs, Yellowstone Park, U.S.A. (Plate 27).

Limestone, or calcium carbonate, when strongly heated, decomposes into *quicklime* (calcium oxide) and carbon dioxide. This process, which is known as the burning of lime, is carried out on a very large scale in rotary kilns as a step, more especially, in the production of slaked lime and mortar.

When water is poured on quicklime, combination takes place and the quicklime is converted into *slaked lime* (calcium hydroxide). So great is the heat evolved in this process that large volumes of steam are produced, and the water may even be made to boil. In the making of *mortar*, the slaked lime is mixed with a certain amount of sand, in order to prevent too great a contraction taking place when the mortar sets; and the setting of mortar depends on the fact that on exposure to the air the slaked lime reacts with the carbon dioxide to form a coherent mass of interlocking crystals of calcium carbonate (limestone).

Slaked lime or calcium hydroxide dissolves sparingly in water, the solution being known as *lime water*. It is used medicinally as a mild alkali.

Calcium carbonate occurs in various forms. *Chalk* and *limestone* have been formed from the shells or skeletons of marine organisms, deposits of which have become compacted under pressure; and *coral* is built up by the minute coral polyp. *Marble* represents a limestone which has been transformed by heat and pressure into a mass of small crystals. Large transparent crystals of calcium carbonate are also found as *calcite* or *Iceland spar*. This material has the property of double refraction, as it is called, so that an object, printed matter for example, appears double when viewed through a crystal of Iceland spar (Plate 28).

Pearls, also, consist essentially of calcium carbonate deposited, layer on layer, by the oyster on a particle of sand, or other foreign body. Since all carbonates are decomposed by acids, with evolution of carbon dioxide, pearls will be destroyed if allowed to come in contact with acid liquids, *e.g.* vinegar. In this connection one may recall the story told by Plutarch of how Cleopatra, wishing to impress Antony with her wealth and magnificence, wagered that she could spend the equivalent of £150,000 on a single meal. The wager having been accepted, Cleopatra, who was wearing two pearls each equal to half the sum, detached one and dropped it into a cup of vinegar. The pearl quickly disappeared and she then drank the liquid. She was proceeding to do likewise with the second pearl when she was restrained, it being decided that the wager had already been won.

CLAY

Among the most important of the naturally occurring minerals are those double silicates of an alkali metal (sodium or potassium) and aluminium which are known as *felspars*. These compounds, present so abundantly in granites, while insoluble in water, are attacked by the atmospheric carbonic acid and undergo decomposition with formation of alkali carbonate and aluminium silicate; and this aluminium silicate, in a hydrated state and known as *kaolinite*, is the main constituent of kaolin or white china clay. To this material also is mainly due the plastic properties of the common clays in which the kaolinite is mixed with various impurities.

Clay is, in our modern no less than in the ancient civilizations, a material of great importance, and is used for the production not only of building materials but also of porcelain, stoneware and earthenware. This importance it owes mainly to the fact that it forms, with water, a plastic mass which becomes hard and stone-like when heated to a high temperature. Clay is also used in the manufacture of cement.

In the manufacture of *porcelain or china*, pure white clay is mixed with the requisite amount of ground felspar and quartz, known as 'frit,' and the soft, plastic mass is then formed into the desired shape. On being heated in a kiln to a temperature of about 1200° C. (say, 2190° F.), the clay loses water and passes into an anhydrous silicate, $3Al_2O_3, 2SiO_2$, and the felspar fuses and dissolves the quartz. A glass is thus formed which binds the mass together and renders it non-porous and non-absorbent of water. The mass also becomes translucent, in proportion to the amount of glassy material present.

In the production of *stoneware*, the fusion of the 'frit' is not so complete, so that the body of the ware, although non-porous, is not translucent.

In the manufacture of *earthenware*, the ware is fired at a lower temperature and very little vitreous material is formed. The body of the ware, therefore, is porous. This is known as *bisque* or 'biscuit' ware. When pure materials are employed, such earthenware is largely used as table-ware. After the ware has been fired, it is coated with ground felspar, or other fusible silicate, and again heated. A glassy film or glaze is thereby formed on the surface of the ware.

Clay also finds a very important application at the present day for the production of *Portland cement*, a material which owes its name to its resemblance to Portland stone. Clay and limestone (or other form of calcium carbonate) are mixed together so as to give the proper proportions of lime, alumina and silica, and the mixture is then ground to a fine powder and heated in long, rotary kilns to the point of incipient fusion. The partially fused mass, which consists essentially of a mixture of calcium silicate and calcium aluminate ($3CaO, Al_2O_3$), is ground and constitutes the Portland cement of commerce. The pasty mass formed by mixing with water has the property of setting hard, even under water. A small quantity of gypsum is added to the ground cement in order to delay the early or initial setting.

Concrete, now so largely employed for building purposes and for road making, is a mixture of cement with sand or gravel.

Chapter 10

ELECTRICITY AND CHEMISTRY

In a previous chapter it was sought to point out and to emphasize that a chemical reaction must no longer be considered as involving merely a transformation of material but also a flow of energy; and it was also claimed that one of the chief characteristics of the scientific advance during the past hundred years has been the manner in which and the extent to which the different forms of energy have been transformed and utilized. In our study of the subject of combustion we had a glimpse into that branch of science, thermo-chemistry, which deals with the relations which exist between chemical energy and heat energy; and from the present chapter, it is hoped, the reader will gain some insight into the relationships which obtain between chemical energy and that other form of energy, electrical energy, the utilization of which is so notable a feature of modern times.

The birth of electro-chemistry, as this twin branch of science which deals with the relations between electricity and chemistry is called, may be dated from the time when, in 1791, the Italian anatomist, Luigi Galvani, observed the convulsive twitching of the muscle of a freshly dissected frog, each time the muscle and nerve were connected by two different metals. It was a humble birth, surely, for a science which has revolutionized the world, which has made practicable the telegraph, telephone and 'radio,' and has supplied mankind with many materials both of ornament and of use.

If it is to Galvani that we owe the observation in which electro-chemistry found its birth, it is to his fellow-countryman. Alessandro Volta,[1] Professor of Physics in the University of Pavia, that the science owes its further development. Rightly interpreting the muscular contraction of the frog's leg as being due to the current of electricity which is produced whenever contact is made between two different metals separated from each other by a liquid conductor, Volta constructed an apparatus whereby a continuous current of electricity could be obtained through the transformation of chemical energy into electrical energy. When a strip of copper and a strip of zinc are partially immersed in a solution of sulphuric acid, Volta found that on connecting the free ends of the metals by means of a conducting wire, a current of electricity is obtained. By connecting a number of such cells together, so that the copper plate of one was joined to the zinc plate of the next, Volta built up a battery—the famous *couronne de tasses*, or crown of cups—with which effects of the most notable character were obtained; and the voltaic cell, as it was called, was the scientific sensation and curiosity of the end of the eighteenth and the beginning of the nineteenth century. Similar but more efficient cells were constructed by others, and the effect of the electric current was tried on a great variety of substances, with the result that, under the guiding genius of Sir HUMPHRY DAVY, the alkali metals, sodium and potassium, were isolated for the first time in 1807, by passing a current of electricity through molten caustic soda and molten caustic potash.

---

[1] The intimate connection of Volta with electricity is held in remembrance by the use of the term *volt* as the unit of potential (or *voltage*) of an electric current.

These two metals, SODIUM and POTASSIUM, which are doubtless unfamiliar to most people, are silvery-white in colour, and very lustrous. When exposed to the air, however, they tarnish immediately, owing to the readiness with which they react with the water vapour in the air. They are soft and of a cheese-like consistency, so that they can be readily cut with a knife. When brought into contact with water they decompose it with great vigour, with production of hydrogen and formation of caustic soda and caustic potash. Such, in fact, is the vigour of the reaction that the hydrogen which is liberated may become ignited and burn, with a yellow flame in the case of sodium, and a violet flame in the case of potassium. These metals find no application in ordinary life,[1] but are used in considerable quantities in chemical manufactures.

Sodium cyanide, NaCN, which is extensively used in the extraction of gold (p. 88), is produced industrially by passing ammonia over a heated mixture of sodium and carbon:

---

[1] Sodium vapour lamps are frequently used for the lighting of streets and highways.

$$2Na+2C+2NH_3=2NaCN+3H_2.$$

The hydrogen formed in the process can be used in the synthesis of ammonia (p. 131) or for other purposes.

Such was the beginning of man's triumphant success in transforming chemical into electrical and electrical into chemical energy. Important as were the results obtained by the use of the voltaic cells, when regarded from the purely scientific point of view, the cost of working the cells was very considerable, and it was not, therefore, until the introduction of the dynamo (made possible by the scientific researches of Faraday) that the industrial application of electricity became practicable. With the aid of the engineer and by means of the dynamo it has now become possible to obtain a cheap supply of electrical energy, more especially by harnessing the great waterfalls of the world. The *couronne de tasses* of Volta has been replaced by multitudes of humming dynamos; and in place of the few globules of metallic sodium which Sir Humphry Davy succeeded, with much difficulty, in isolating, that and many other substances are now produced by hundreds and thousands of tons in the electrochemical factories of the world.

One of the earliest industrial uses to which electricity was put, was to the coating of cheaper with more expensive or more resistant metals, by a process known as *electroplating*, a process which has been widely used from before the middle of last century. At the present day the process is largely applied to the plating of metals not only with gold and silver, but of silver with rhodium (p. 89) and of copper and steel with nickel and with chromium, metals which are much used on account of their white colour and resistance to atmospheric tarnishing and corrosion. For the galvanizing of steel, especially for the continuous galvanizing of steel wire, hawsers, etc., and also for the production of tin-plate the process of electrodeposition of the zinc and tin is extensively applied; and steel nuts, bolts, screws, etc., which are to come in contact with light alloys are electroplated with cadmium. Not only pure metals, but also alloys, *e.g.* speculum (tin-copper alloy), bronze, tin-lead alloy, etc., can be deposited from a solution containing salts of the two metals.

In principle the process is comparatively simple, and consists in passing a current of electricity through a solution of a salt of the metal with which the article is to be plated; but in order that we may understand the process better, we must consider the nature of the liquids which conduct the electric current.

When one places in a vessel containing pure distilled water the ends of two wires which are connected with an electric-lighting circuit and lamp (Fig. 17), the lamp remains dark. The electrical circuit is broken by the water which is a non-conductor of electricity. If to the water one adds cane sugar, glycerine, or alcohol, the lamp still gives forth no light, for the solutions of these substances do not conduct the electric current. But if one dissolves in the water even a very little common salt, washing-soda, or hydrochloric acid, the lamp at once lights up, showing that the flow of electricity is no longer interrupted by the liquid. In the same way other substances soluble in water may be tested, and it will be found that substances can be divided into two classes, those that yield solutions which conduct electricity, and those that yield solutions which do not conduct electricity. Substances belonging to the former class are called *electrolytes*, substances belonging to the latter class, *non-electrolytes*. Sugar is a non-electrolyte; salt is an electrolyte. Similarly, all the substances known as *acids*, which have a sour taste and the property of turning red a blue solution of the vegetable colouring matter called litmus, are electrolytes; all the substances, also, known as *alkalis*, which have the opposite property of restoring the blue colour to solutions of litmus which have been reddened by acids; and all the substances known as *salts*, which are formed by the combination of acids and alkalis—all these substances, acids,

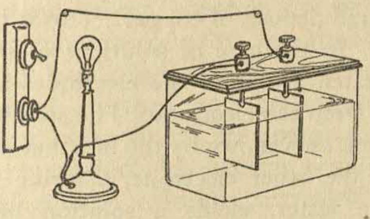


FIG. 17.—CONDUCTIVITY OF SOLUTIONS FOR ELECTRICITY

alkalis and salts, are electrolytes, and yield solutions which conduct the electric current.

When an electric current passes through the solution of an electrolyte, even the most superficial observation will teach us that a liquid conductor differs from a metallic one. In the latter case, no apparent change may take place, but in the former there is a very obvious decomposition of the conducting solution. This process of decomposition by an electric current is known as *electrolysis*. If one dips into a solution of copper sulphate, for example, two bright wires or plates of platinum which are connected to the poles of a battery, the solution of copper sulphate is decomposed and one sees that the surface of one of the *electrodes* (as the portions of the metallic conductor dipping into the solution are called) immediately becomes coated with a bright rose-coloured deposit of copper. This is the process used in electroplating. In the case of solutions of sodium chloride, hydrogen is liberated at one of the electrodes and can be seen rising in bubbles from the electrode. The solution also acquires an alkaline reaction, as is shown by the fact that it turns reddened litmus blue. At the other electrode, chlorine is set free and, dissolving in the water, yields a solution having bleaching properties, as is shown by the fact that it discharges the colour of a litmus solution. Whenever, therefore, an electric current passes through a conducting solution, there is a movement of electrically charged matter through the liquid—charged particles of copper, or hydrogen, or chlorine, for example—and some of these particles move towards the one electrode, others towards the other electrode.

This conclusion was reached early last century by that great natural philosopher, MICHAEL FARADAY, who called the electrically charged moving particles which thus conveyed the electricity through the solution, by the happily chosen Greek term *ions* (*i.e.* wanderers); and this term is still retained.

During a great part of last century, the conductivity of electrolytes in solution was the subject of much discussion. Faraday, and many others after him, assumed that the molecules of an electrolyte are decomposed *by the electric current* into positively and negatively charged particles—the ions—which then move in opposite directions through the solution. This view was later shown to be incorrect, and in 1886 the Swedish physicist, SVANTE ARRHENIUS, put forward the very revolutionary view that some of the molecules of an electrolyte, when dissolved in water, break up *spontaneously* into ions, and that the fraction of the molecules which undergoes this process of ionization increases as the solution is made more and more dilute. Thus, the molecules of common salt, or sodium chloride, for example, were supposed to break up in solution into positively charged sodium atoms or sodium ions, Na^+, and negatively charged chloride ions,[1] Cl^-; and these ions were regarded as leading a free and independent existence in the solution, each exhibiting its own properties and showing its own chemical reactions. This *theory of electrolytic dissociation*, as it was called, proved to be, in many respects, exceedingly satisfactory, and was very generally accepted.

In one important respect, however, the theory of Arrhenius, when applied to solutions of salts, was found to be defective. As we shall learn more fully in *Chapter* 17, the molecule of sodium chloride is formed by the electrostatic attraction between a sodium atom which has acquired a positive charge and a chlorine atom which has become negatively charged. In the molecule of sodium chloride, therefore, the sodium and chlorine are already present as electrically charged particles, *i.e.* as *ions.* Solution of salt in water, therefore, does not, as Arrhenius thought, bring about the formation of ions; solution merely brings about a diminution of the force of attraction between the electrically charged sodium and chlorine atoms (ions), and makes it possible for them to move about freely in the solution. A similar freedom of movement is made possible by melting the salt, and fused sodium chloride and fused sodium hydroxide are also found to conduct the electric current, owing to the presence of ions.

As in the case of sodium chloride, so also in the case of other salts, the ions are pre-existent in the molecules, and solution in water merely makes freedom of movement possible.

The same explanation is valid also in the case of the metal hydroxides, such as sodium and potassium hydroxides. These all contain the hydroxide ion, OH^-, and solutions of these hydroxides, therefore, all contain this ion. It is, in fact, to the presence of hydroxide ions in solution that the general properties of alkalis are due.

---

[1] These ions are generally called chloride and not chlorine ions because they are present in salts known as chlorides, *e.g.* sodium chloride.

The theory of Arrhenius, however, does apply to acids, such as hydrochloric acid, which do not conduct the electric current in the liquid state. Ion formation takes place only on solution, and one may assume the occurrence of a reaction such as $HCl + H_2O = H_3O^+ + Cl^-$, the ion H_3O^+ being a hydrated hydrogen ion, $H^+.H_2O$. All acids in solution give rise to this ion, and the so-called acid properties of a solution are really due to the presence of hydrogen ion.

In the light of what has just been stated, the fact that the solution of a salt, an acid or an alkali in water conducts the electric current, becomes readily intelligible. These solutions contain free, positively charged *cations* (hydrogen or metal ion), and free, negatively charged *anions* (hydroxide ion, OH^-, or acid ion, Cl^-, NO_3^-, etc.). When, therefore, two electrodes are placed in the solution of an electrolyte and connected with an electric battery, the positively charged electrode (the *anode*) attracts the negatively charged ions, the anions; and the negatively charged electrode (the *cathode*)[1] attracts the positively charged ions, the cations. These anions and cations move in opposite directions through the solution, and give up their charges at the electrodes; they transport or convey the electricity through the solution, and it is this movement or procession of electrically charged particles that constitutes what is called the electric current in the solution.

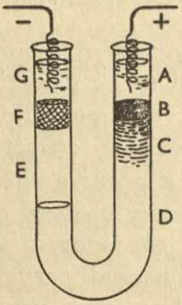


FIG. 18.—MIGRATION OF IONS

This explanation of the passage of a current through a solution is not a mere speculation, not a mere phantasy, for it is easy to demonstrate not only that there is a movement of the ions through the solution, but also that the ions move with different velocities. There is a pretty experiment by which one can make this clear. Into the bend of a tube bent into the form of the letter U (Fig. 18) is poured a solution of potassium chloride to which sufficient gelatin has been added to make the liquid set to a jelly; and the solution is also coloured red by the addition of a substance called phenolphthalein and a drop or two of alkali. (Phenolphthalein is a colourless substance which yields a deep-red colour with alkalis, or solutions containing hydroxide ions; and the red colour is again destroyed by addition of acids, or solutions containing hydrogen ions.) After the solution in the bend of the tube has set, a further quantity of the same coloured solution is poured into one limb of the tube (D), while into the other limb (E) is poured the same solution after it has been decolorized by the addition of the requisite amount of acid.

---

[1] The terms ion, anion, cation, anode and cathode introduced by Faraday were suggested to him by W. Whewell, Master of Trinity College, Cambridge.

Above this colourless layer of gelatin is placed a quantity of a mixed solution of caustic potash (potassium hydroxide) and potassium chloride (G), while in the other limb of the tube is placed a mixed solution of hydrochloric acid and copper chloride (A). An electric current is now passed through the solutions in the tube, by placing a platinum wire connected with the positive pole of a battery in the solution of hydrochloric acid and copper chloride; and a platinum wire connected with the negative pole of the battery in the solution of caustic potash and potassium chloride. After the current has passed for some time it is found that the hydrogen ions (from the hydrochloric acid), moving from the positive towards the negative electrode, have decolorized the reddened phenolphthalein, and have produced, therefore, a colourless band (C) of a certain depth. The blue-coloured copper ions (from the copper chloride), which move in the same direction as the hydrogen ions but with a slower speed, follow on into the colourless band produced by the hydrogen ions, and give a blue colour to the gelatin (B). In the other limb of the tube, the hydroxide ions (from the caustic potash), moving from the negative to the positive electrode, pass into the colourless gelatin and produce with the phenolphthalein there a red-coloured band (F). This band is deeper than the blue band produced by the copper ions, but not so deep as the colourless band produced by the hydrogen ions, from which one concludes that the hydrogen ions move faster than the hydroxide ions, and the latter faster than the copper ions.

Acid-alkali Indicators. The substance phenolphthalein, to which reference has just been made, belongs to a group of substances known as acid-alkali indicators, because they indicate, by the colour which they assume in a solution, whether that solution is acid or alkaline.

In water and in all aqueous solutions, hydrogen ions and hydroxide ions exist together in a very low concentration. In pure water these ions are present in equal concentration, and the liquid, therefore, is neither acid nor alkaline. It is *neutral.* If, in an aqueous solution, the concentration of hydrogen ion is greater than the concentration of hydroxide ion, the solution is said to be acid; and if the concentration of hydroxide ion is greater than the concentration of hydrogen ion, the solution will be alkaline.

The vegetable colouring matter, litmus, when added to an acid solution, shows a red colour; but when added to an alkaline solution, the colour is blue. Phenolphthalein, as has been mentioned, is colourless in acid solution, and red in alkaline solution. Methyl orange shows an orange or red colour in acid solution and a yellow colour in alkaline solution. Other substances, also, show a difference of colour in acid and alkaline solutions and can therefore be used as acid-alkali indicators. Moreover, these indicators show a change of colour at different concentrations of hydrogen ion; and it is therefore possible, by adding different indicators to an aqueous solution, to tell what is the concentration of hydrogen ion present in the solution, or to tell what may be called the degree of acidity (or alkalinity) of the solution. The degree of acidity, or concentration of hydrogen ion, is of much importance in many chemical and industrial operations, and in agriculture (acidity of the soil).

The degree of acidity of a solution is now commonly expressed in terms of what is called the pH value.[1] Pure water, in which the concentration of hydrogen ion is 1×10^{-7} gram per litre, has the pH value of 7.00. Solutions which have a pH value less than 7.0 are acid solutions; and the *smaller* the pH value, the greater is the concentration of hydrogen ion, or the greater is the degree of acidity of the solution. When the pH is greater than 7.0, the solution is said to be alkaline.

Voltaic Cells.—Not only does the theory of ionization afford an explanation of the process of electrolysis, whereby electrical energy is transformed into chemical energy, or the potential energy of chemically reactive substances, but it helps us also to understand the reverse process of the transformation of chemical energy into electrical energy, as it occurs in the different voltaic cells.

---

[1] In mathematical terms, $\text{pH} = \log \frac{1}{[\text{H}^+]} = -\log [\text{H}^+]$, where $[\text{H}^+]$ is the concentration of hydrogen ion expressed in grams of hydrogen ion per litre of solution.

One of the best known cells, formerly widely used for working telephones and electric bells, is the Leclanché cell (Fig. 19). This very simple cell consists of a jar containing a solution of sal-ammoniac (ammonium chloride), in which are immersed a zinc rod and a plate of graphite packed in a porous pot with granules of graphite and black oxide of manganese (manganese dioxide). The porous pot also contains a solution of ammonium chloride. When the cell is in use, zinc atoms readily give up electrons, or negative charges of electricity (*Chap.* 17), and pass into solution as positively charged zinc ions. The electrons given up by the zinc atoms pass through the metallic conductor to the graphite plate where they neutralize the positive charge on the ammonium ions (NH_4^+) formed by the ionization of ammonium chloride, and so give rise to the uncharged group of atoms, ammonium (NH_4). This group cannot exist as such and immediately reacts with the water (just as sodium does), with production of ammonium hydroxide (NH_4OH) and hydrogen. This hydrogen, however, is oxidized to water by the oxide of manganese, and so is prevented from forming a non-conducting layer on the electrode, and thereby stopping the current. The electrode is thereby 'depolarized' as it is said. When the cell becomes exhausted, its activity can be renewed by replacing the spent liquid by a fresh solution of ammonium

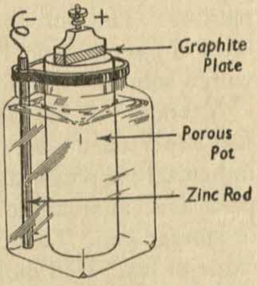


FIG. 19.—LECLANCHÉ CELL

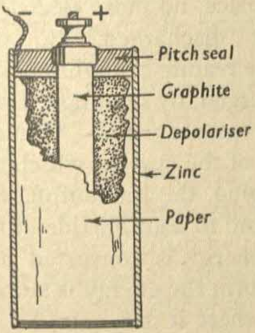


FIG. 20.—DRY CELL

chloride. The Leclanché cell has an electromotive force of 1·5 volts.

The Leclanché type of cell has passed into very widespread use owing to its modification to form the common dry cell, used in torches, radio-sets, etc. In this cell there is a zinc container which also acts as the negative pole of the cell, and inside this is placed the graphite plate or rod with its depolarizing packing. The latter is separated from the zinc container by a layer of paper which, like the whole contents of the cell, is soaked with a solution of ammonium chloride (Fig. 20).

Although, as has been said, the much more efficient dynamo has superseded the voltaic cell as a source of electricity for industrial purposes, there is one cell which occupies an important place as an auxiliary to the dynamo. This is the lead accumulator, or storage cell. This cell consists of plates of lead and of brown oxide of lead, lead dioxide as it is called, immersed in a solution of sulphuric acid of specific gravity about 1·30. On joining these two plates by means of a conductor, a current of electricity flows through the conductor from the lead dioxide plate to the lead plate.[1] The chemical reaction which yields the energy which is transformed into electricity, is the conversion of the lead and lead dioxide into lead sulphate: $Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$. When this change has taken place, no more electricity is given out; the cell is 'run down' or 'discharged.' But this cell has the great advantage that it can be readily brought back to its former condition, can be readily recharged, by sending a direct current of electricity—obtained, say, from a dynamo—through the cell in the opposite direction to that of the current which the cell itself gives. In the process of charging, the lead sulphate is converted to lead at the negative pole, and to lead dioxide at the positive pole. In this way, electrical energy is converted into potential, chemical energy; and in this form the energy is stored, and is available for use just when and where it is required.

The process of charge and discharge can be followed by means of a *hydrometer* which enables the specific gravity of the acid to be determined. When the cell is being discharged, sulphuric acid is used up to form lead sulphate, and the specific gravity of the solution falls; but when the cell is being charged, sulphuric acid is returned to the solution and the specific gravity increases. In the fully charged cell the specific gravity should be about 1·30; when the cell is discharged, the specific gravity falls to 1·15.

---

[1] Conventionally, positive electricity is said to flow from the lead dioxide plate to the lead plate. Actually, in the external circuit there is a flow of negative electricity (electrons) from the lead to the lead dioxide plate.

The lead storage cell is one which has now a multitude of uses, such as giving current for electric lighting on a large scale (as an auxiliary to the dynamo), or in portable hand-lamps; for energizing the self-starters of motor cars; and in many other cases where a readily transported supply of energy is desired.

Another storage cell, possessing a number of advantages over the lead accumulator, is the nickel-iron cell which is sometimes known as the Edison cell. In this cell the active mass of the positive plates consists essentially of nickelic hydroxide, $Ni(OH)_3$, or nickelic oxide, Ni_2O_3, in a hydrated form, and this is mixed with powdered graphite to give increased conductivity. The active mass of the negative plates is finely divided iron. The electrolyte is a solution of potassium hydroxide of specific gravity 1·190. The active materials are contained in pockets in nickel steel plates and are formed under a pressure of 200 tons.

When this cell is yielding current, the nickelic oxide on the positive plate is reduced to the lower oxide, nickelous oxide (NiO), in a hydrated form, or to nickelous hydroxide, $Ni(OH)_2$; and the iron on the negative plate is oxidized to the oxide (FeO), or hydroxide, $Fe(OH)_2$. The chemical change which takes place, therefore, may be represented by the equation: $Fe + 2Ni(OH)_3 = Fe(OH)_2 + 2Ni(OH)_2$. The charged cell has a voltage of 1·35 volts.

When the cell has become discharged, it can be recharged by passing a current through the cell in a direction opposite to that of the current given by the cell. Thereby, the nickelous hydroxide is oxidized to nickelic hydroxide, and the iron hydroxide is reduced to metallic iron.

The nickel-iron accumulator has a lighter weight and greater robustness than the lead accumulator, and it does not undergo deterioration, as the lead accumulator does, when left in a discharged state. It is, in fact, much less liable to damage by careless treatment, and has a longer life.

The nickel-cadmium cell is similar to the one just described. Its electromotive force is 1·25 volts.

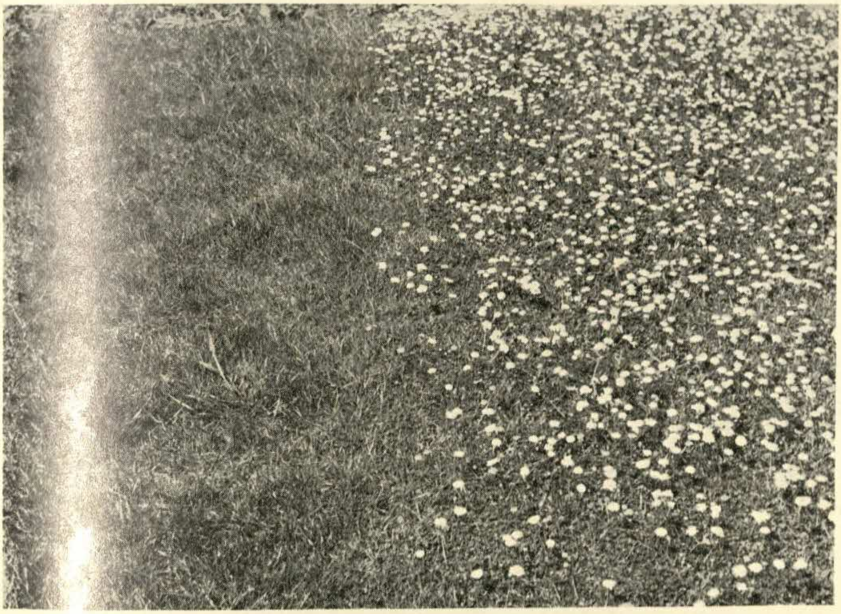
TUTE OF EDUCATION FOR WOMEN
Dept. of Extension
SERVICE.
CALCUTTA-27

The application of electricity to chemical manufacture produced an industrial revolution. Not only have electrochemical processes more or less completely displaced the older chemical methods employed for the manufacture of such substances as caustic soda and of chlorine, or for the isolation of such metals as sodium, potassium, calcium, magnesium and aluminium, but they have made possible also the discovery and economic production of many new substances of great value.

One of the earliest applications of electricity, we have seen, was to the electroplating of metals by a process of electrolysis. By this process, also, metals can be obtained in a state of great purity, and the method is now used for the refining of certain metals, more especially of copper. The crude copper, obtained by smelting its ores, contains a number of impurities, among which are silver and gold, sometimes in not inconsiderable quantities. This crude copper, cast into plates, is made the anode in a bath of copper sulphate solution, while a thin plate of pure copper is made the cathode. When the electric current is passed, copper is deposited in a pure state on the cathode, from which it can afterwards be readily stripped, whereas the copper of the anode passes into solution by combining with the sulphate ions which are discharged at the anode. Some of the impurities present in the copper may also dissolve and accumulate in the solution; other impurities, however, such as silver and gold, do not dissolve, but fall to the bottom of the bath as a slime or mud, known as the 'anode mud,' from which the valuable metals are extracted by suitable methods.

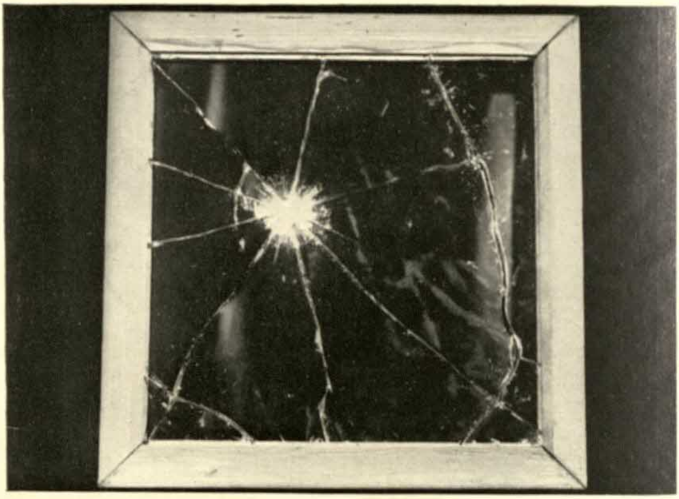
By this simple process, the purest commercial copper, so-called 'electrolytic copper,' is obtained, and is used mainly for electrical purposes. The importance of pure copper in this connection is due to the fact that the conductivity of copper for electricity is greatly diminished even by small amounts of impurity.

The electrolytic preparation of sodium hydroxide or caustic soda and of chlorine depends on the electrolysis of a solution of sodium chloride or common salt. When a pure caustic soda is desired, the electrolysis is carried out in a large covered-in tank filled with a solution of sodium chloride into which dip graphite electrodes. These serve as anodes. At these electrodes, when the cell is in action, chlorine is evolved and passes away through a



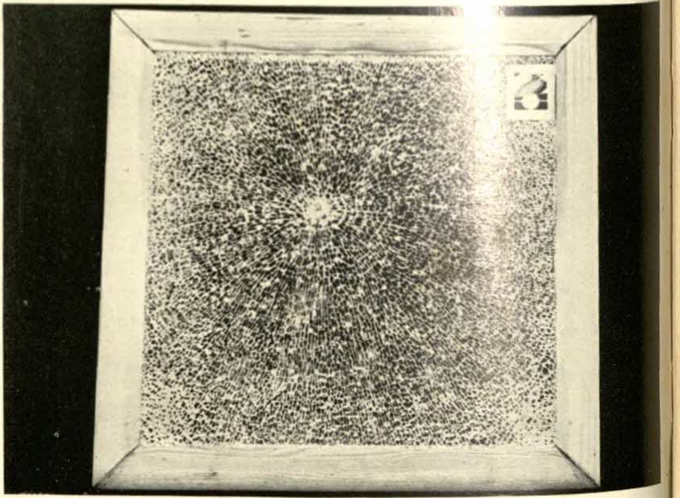
19. SELECTIVE WEED CONTROL
The left-hand side of the lawn has been treated with selective weed-killer (2:4–D)

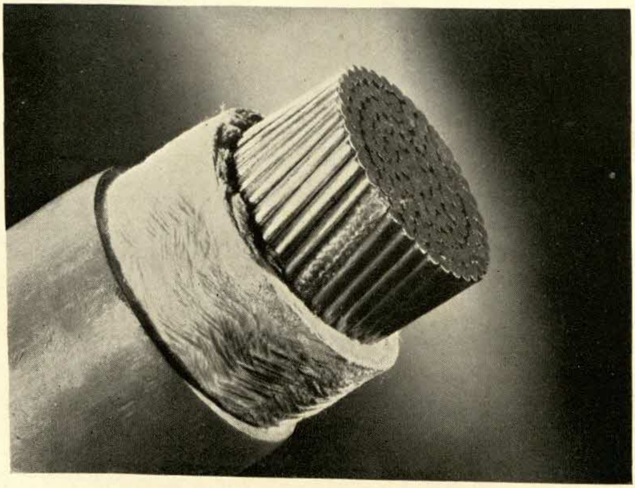
20. CASTLE GEYSER, YELLOWSTONE PARK



21. CRACKING OF ORDINARY PLATE GLASS

22. CRACKING OF 'ARMOURPLATE' GLASS





23. FIBREGLASS INSULATION OF ELECTRIC CABLE

pipe in the roof of the tank. Along the floor of the cell mercury is allowed to flow in a slowly moving stream. This forms the cathode, and the sodium which is here set free dissolves in the mercury. The solution of sodium in mercury flows out at the end of the tank and is treated with pure water. The sodium reacts with the water, giving rise to hydrogen and a solution of caustic soda, and the mercury is passed through the cell again.

When the electrolysis is carried out mainly for the production of chlorine, other types of cell are frequently used.

Solid caustic soda is obtained from the solution by evaporating off the water. It forms a white very hygroscopic solid which undergoes deliquescence or becomes moist when exposed to the air. It is readily soluble in water, and the solution has the soapy feeling characteristic of alkalis. Large quantities of caustic soda are used in the manufacture of soap.

In the electrolysis of solutions of sodium chloride for the production of sodium hydroxide, the hydrogen which is produced must be considered as a by-product and is sometimes discarded. To an increasing extent, however, the hydrogen and chlorine are now caused to combine together—hydrogen burns in chlorine—so as to form hydrogen chloride. On dissolving this gas in water, a pure hydrochloric acid is obtained.

The electrolytic process is also extensively used for the industrial production of pure hydrogen and oxygen (Plate 29). In this case, a solution of caustic soda is generally employed as the electrolyte. When the current is passed through the solution, hydrogen is liberated at the cathode, and oxygen is liberated at the anode.

FLUORINE.—The great importance attaching to the production of the compound, uranium hexafluoride (*Chap.* 17), led to the intensive investigation of the gaseous element, fluorine, first isolated by the French chemist HENRI MOISSAN in 1886. The element, although for long almost entirely a laboratory curiosity, is now produced industrially by the electrolysis, in copper or steel cells, of the compound $KF,3HF$, at a temperature of 80°–100° C. Fluorine is evolved at the anode and may be stored in steel or nickel cylinders.

Fluorine is the first member of the important family of elements known as the *halogens* (salt-formers), the other members being chlorine, bromine and iodine. It is chemically the most reactive of all the elements. It combines with hydrogen with explosive violence to form hydrogen fluoride, HF; and by introducing a jet of fluorine into hydrogen an intensely hot flame, which can be used for welding copper and nickel, is obtained.

Fluorine is now used in the production of many compounds, especially compounds of carbon, which are of extreme scientific interest. A number of them, also, are of great industrial importance as solvents, as high-temperature lubricants, as electrical insulators, etc. The compound dichlorodifluoromethane, CCl_2F_2, known as *freon*, is now very widely used as the cooling agent in refrigerators.

A solution of hydrogen fluoride in water, *hydrofluoric acid*, is used for etching glass.

ALUMINIUM.—It has already been pointed out that electrolysis may be applied not only to substances dissolved in liquids but also to substances in the fused state, as in the production of the metals sodium and potassium. One of the most important examples of this is found in the electrolytic production of the metal aluminium. This is the most abundant of all the metallic elements in the world, but it occurs naturally only in the form of compounds, in combination with other elements. So difficult is it to isolate the metal from its compounds by purely chemical methods, that it was not till 1845 that the metal was obtained in the compact form. And it was then merely a chemical curiosity; for any general or industrial application its cost was prohibitive. It is, in fact, only since 1886 that it has become possible, by the application of an electrolytic method, to produce the metal at a reasonable price. The isolation of the metal is effected by the electrolysis of a solution of purified bauxite[1] or oxide of aluminium in molten cryolite (a naturally occurring compound of aluminium with fluorine and sodium, now usually produced artificially), and the entire world's production of the metal is obtained by this means. For the electrolysis, a steel bath, lined with graphite, is used, and this forms the cathode, while large graphite rods dipping into the molten electrolyte form the anode. As the current of electricity passes through the molten mass, aluminium separates out at the cathode and collects in the liquid form at the bottom of the bath, whence it can be run off from time to time. At the anode, the oxygen which is liberated combines with the carbon electrodes, producing the poisonous gas carbon monoxide, which may either escape as such or burn to form carbon dioxide.

---

[1] So called because the mineral was first found near Les Baux in the south of France.

Aluminium now occupies a permanent and ever-growing place in our modern life, the world output of the metal ranking next to that of iron and steel. Not only is it largely employed for cooking utensils and other articles of domestic use where lightness and portability are of importance,[1] but it is also used, as we have seen, for the production of high temperatures by the thermit or alumino-thermic process, and for the isolation of certain metals.

Aluminium is a white, lustrous metal which is highly resistant to corrosion by the gases of the atmosphere, even the atmosphere of large towns, as is shown by the beautiful, gleaming, aluminium figure of Eros which surmounts the bronze Shaftesbury Fountain in Piccadilly Circus, London (Plate 30). This resistance to atmospheric corrosion is due to the rapid formation on the surface of the metal of an invisible film of oxide which protects the underlying metal from further attack. This protective film can be strengthened by making aluminium the anode in the electrolysis of a solution of chromic or sulphuric acid, a process known as *anodizing*. If, during the process of electrolysis, a suitable dye is present in the acid solution, it is taken up and fixed by the aluminium oxide, the metal being thereby coated with a hard, coloured film. This process is used for decorative purposes. By using a suitable yellow dye, a 'surface dyed' metal can be obtained and can be used in making imitation gold cigarette cases, vanity cases, etc.

Aluminium is a good conductor of electricity; weight for weight, indeed, better than copper. Cables of aluminium, therefore, strengthened by a core of steel wire, are being increasingly used for the long-distance transmission of electricity, as in the British National Grid.

As it is an excellent reflector of light, aluminium is extensively used in the making of astronomical and other mirrors (p. 150), reflectors in motor-car headlights, etc. The metal film is best deposited by the method of vaporization in a high vacuum (p. 88).

Aluminium can be rolled into thin foil and, in this form, has to a large extent replaced tin foil as a wrapping material.

---

[1] The specific gravity of aluminium is only 2·7, that of steel about 7·8.

Some of the defects which at one time militated against a more widespread use of the metal, its low tensile strength and softness for example, can be removed to a large extent by admixture with other metals. Some of the alloys formed possess properties of great value. With the metal magnesium, aluminium forms a number of alloys (containing from 1 to 7 per cent. of magnesium) which are even lighter than aluminium itself and have a strength equal to that of brass; and the construction of aeroplanes was revolutionized by the discovery of the alloy *duralumin*, an alloy of aluminium with copper (4 per cent.), magnesium (0·5 per cent.), and manganese (0·5 per cent.). This alloy, while having a tensile strength equal to or greater than steel, has only one-third of its weight. Since duralumin is less resistant than aluminium to atmospheric corrosion and attack by sea-water, the alloy is 'clad' or protected by rolling a thin sheet of pure aluminium on each side of the sheet of duralumin.

Aluminium and alloys of aluminium are increasingly used in textile machinery, farm and dairy equipment, food and chemical industries, internal combustion engines and in all forms of transport where reduction of dead weight is important.

MAGNESIUM.—This lustrous, white metal, which burns in air with a very bright and photographically active light, has long been known on account of its use in pyrotechnics and in the preparation of "flash-light" powders for use in photography. More recently, however, magnesium has come into rapidly expanding use as an industrial metal, the lightest of all the industrial metals, with a specific gravity of only 1·74. Its main use, now, is for the production of 'ultra light' alloys, containing 90 per cent. or more of magnesium. These are employed as structural materials in aircraft and other vehicles, in the upper structures of ships and for castings of various kinds.

The metal, which occurs in nature only in the form of compounds, is produced mainly by the electrolysis of fused carnallite (p. 126), or of magnesium chloride to which potassium chloride is added in order to lower the temperature of fusion. Much of the magnesium chloride used in this process is now obtained from sea-water, in each cubic yard of which there are about 2 lb. of magnesium in the combined state. When sea-water is treated with calcined dolomite (a double carbonate of calcium and magnesium), which gives rise in contact with water to calcium and magnesium hydroxides, a slurry of magnesium hydroxide is formed. When this is calcined and heated with coke in a current of chlorine, magnesium chloride is obtained.

Processes have also been devised for obtaining magnesium by the reduction of the oxide by means of calcium carbide, aluminium, etc.

Magnesium is a metal which has but little strength, but by alloying it with other metals, especially aluminium and zinc, increased mechanical strength is obtained; and the strength can be still further greatly increased by the addition of small amounts of the hitherto but little used metal zirconium.

Magnesium and its alloys find an interesting use as 'sacrificial' metals in the protection against corrosion of iron and steel structures buried in the earth (*e.g.* oil pipe-lines). Plates of magnesium buried in the earth are connected to the pipes by insulated copper wire. Thereby a voltaic cell is formed, with moist earth as electrolyte. Under these conditions the magnesium becomes the anode and corrodes away by giving rise to metal ions; and the iron pipe becomes the cathode and as such cannot corrode or give up metal ions to the earth. A similar device can be used for the protection of domestic water tanks.

Magnesium occurs in nature as the carbonate, *magnesite*, which gives rise, on calcination, to the oxide, *magnesia*. The double carbonate of calcium and magnesium, known as *dolomite*, is abundant and widespread. Magnesium sulphate, which can be formed by the action of sulphuric acid on magnesium oxide or carbonate, is found in various mineral waters. It is known as *Epsom Salt*, and is used medicinally.

Electricity has been turned to important use in chemical industry on account of the ease with which high temperatures can be obtained by means of the electric arc or by passing a current of electricity through a conductor which offers a certain resistance to its passage. As a direct result of the successful application of electricity to the production of high temperatures we owe the industrial production of the valuable abrasives *carborundum* (a compound of carbon and silicon) and *alundum* (aluminium oxide), as well as of *artificial graphite*, which is of great value as a lubricant and as an electrode material in electrochemistry.

Chapter 11

THE COLLOIDAL STATE

WHEN one brings sugar, salt, washing-soda and many other common and familiar substances into contact with water, the solid substance, if present in not too large amount, disappears; it *dissolves*, and a clear liquid is obtained which is called a *solution*. A solution, however, must not be regarded as a compound of the dissolved substance, or *solute*, and the solvent, for the composition of a solution may be varied, whereas the composition of a compound is definite and constant. A solution, rather, is to be regarded merely as a *homogeneous mixture* in which the molecules of the solute, combined it may be with a limited number of solvent molecules, are uniformly distributed throughout and among the molecules of the water, or other liquid, which acts as a solvent. It is a homogeneous mixture of variable composition.

Whatever the nature of the solution process may be, one of the most remarkable facts established by the modern investigation of solutions is the very close analogy which exists between a substance in solution and a gas, an analogy which is illustrated by the property more especially of *diffusion*.

To account for the properties of gases there was developed about the middle of last century a theory known as the *kinetic theory of gases*, which was based on the hypothesis that the molecules of a gas are in perpetual and rapid motion, darting about in straight lines with the speed of something like a mile a second, colliding ever and anon, some eighteen thousand million times a second, with other molecules, and pursuing, therefore, as the result of these collisions, a very zigzag course. It is by virtue of this motion inherent in the molecules that a gas can distribute itself or diffuse throughout a room, and can fill completely the space, however large that space may be, which is offered to it. In the case of liquids the same inherent motion of the molecules, and therefore the same power of diffusion, exists; but the process now takes place more slowly, for the molecules of the liquid are packed more closely together, and the mutual collisions are therefore more frequent. The forward progress of a molecule is therefore very slow, like that of a man who might try to pass through a dense and jostling crowd. That diffusion does take place can be easily demonstrated by gently pouring a layer of pure water on to a solution of some strongly coloured substance, such as copper sulphate or potassium dichromate. After some time it will be found that the coloured substance has diffused upwards some distance into the water. The experiment may be made more easily by dissolving in water sufficient gelatin to make a firm jelly, and then placing a piece of this jelly in the coloured solution. After a few hours it will be found that the coloured substance has penetrated some distance into the jelly.

Even when the solution is separated from pure water by a membrane of parchment paper or by an animal membrane (*e.g.* pig's bladder), diffusion takes place just the same, as can be shown by enclosing the solution of copper sulphate in a tube of parchment paper which is then immersed in water. Very soon the presence of the copper sulphate in the water outside the membrane will be detected.

During the sixties of last century this diffusion of dissolved substances through a parchment paper or animal membrane was studied by THOMAS GRAHAM, a native of Glasgow, who later became Professor of Chemistry in University College, London, and Master of the Mint. As a result of his investigations, Graham found that although certain substances pass through a membrane of parchment paper, other substances do not do so. Since the substances, *e.g.* sugar or salt, which pass through this membrane were such as generally crystallize well, whereas those which do not pass through, *e.g.* starch, gelatin, glue, were believed to be amorphous and non-crystallizable, Graham divided substances into the two classes, *crystalloids* and *colloids* (from the Greek *kolla*, glue); and this distinction was one which was long maintained. From a practical point of view, in any case, this distinction was of importance, for, as Graham showed, if a mixture of crystalloids and colloids is placed in a parchment cell and immersed in water, the crystalloids, but not the colloids, diffuse out into the water. In this way a separation of crystalloid from colloid can be effected by a process to which Graham gave the name of *dialysis*, a process used universally at the present day for the preparation of colloids free from crystalloids.

Appropriate as Graham's classification of substances appeared at the time, investigation has shown that it cannot be retained. The terms colloid and crystalloid can now no longer be employed to connote definite and different *kinds* of substances, but only different *states* of matter; for it is now recognized that the distinction between crystalloids and colloids is to be found in the degree of dispersion or subdivision. The term 'colloidal state' of matter is now applied to that range of subdivision of matter which lies between the limits of the microscopically visible and the molecular state.

That this particular range of subdivision of matter should be singled out for special study is justified by the fact that matter in the colloidal state possesses properties which are not exhibited, or are not exhibited so markedly, either by molecular matter or by the grosser microscopic particles. Matter in the colloidal state, moreover, plays a very important part in almost every field of human activity—in agriculture and in the tanning of leather, in the working of clay, in the production of rayon, in the dyeing of textile fibres, etc. It is also responsible for the blue of the sky and the blue of the eye, and matter in the colloidal state has been chosen by Nature as the vehicle of life.

Since the term colloidal refers only to a certain degree of dispersion or subdivision, colloidally dispersed matter may exist in the solid, the liquid or the gaseous state, and the medium in which the particles are dispersed (the so-called dispersion medium) may also be solid, liquid or gaseous. In this way one obtains colloidal suspensions, emulsions, smokes, mists, etc. In the present discussion we shall be concerned mainly with those systems in which water is the dispersion medium.

While it could be inferred from the experiments of Graham that the apparently homogeneous colloidal solutions or colloidal *sols*, as they are called in order to distinguish them from true solutions, are in reality heterogeneous, the question arises how this can be proved. The answer is that even if one cannot see the particles themselves their presence can be detected by what is known as the *Tyndall Phenomenon*.

When the air of a room is bathed in a uniform light no particles are seen, but if sunlight be allowed to pass through a hole in the shutters of a darkened room one sees a diffused light, the sunbeam made visible, in which the larger dust particles are seen to

> 'Glitter like a swarm of fireflies, tangled in a silver braid.'

The diffused light also is due to particles which are large enough to reflect and scatter the waves of light, although too small to be seen as separate individuals by the eye. So also, by means of this 'Tyndall phenomenon,' the presence of particles in a colloidal sol can be detected. If a beam of light is passed through pure water or through a solution of salt, the path of the beam is invisible; the liquid is 'optically empty.'[1] But if the beam is passed through a colloidal sol the path of the beam is traced by a diffused light, like the sunbeam in a darkened room.

From this 'Tyndall phenomenon,' then, one learns that particles which may be too small to be seen in the ordinary way, may be detected if only the light reflected or dispersed by the particles, and not the direct rays from the source of light, is allowed to enter the eye. And it is clear that if, instead of the unaided eye, one employs a microscope to examine the scattered light, the range of vision will be extended, and it will be possible to detect, although not actually to see in their own shape and colour, particles which are much smaller than can be seen when the microscope is used in the ordinary way. On the basis of this principle there has been devised an arrangement known as the *ultra-microscope*, by means of which not only the heterogeneity of colloid sols can be detected, but also the number of particles in a given volume of the sol can be determined. The arrangement is shown diagrammatically in Fig. 21. A powerful beam of light, instead of being directed into the microscope through the liquid to be examined, is sent horizontally into the liquid, at right angles to the line of vision through the microscope. If the liquid under examination is optically empty, the field of view in the microscope will appear quite dark; but if particles are present in the liquid, the light will be reflected and dispersed, and the minute points of light thus produced will stand out as bright specks against a dark background, in the field of view of the microscope.

---

[1] Owing to the presence of floating particles even in filtered water, the 'Tyndall phenomenon' will be observed with ordinary pure water. Special precautions must be adopted to free the water from all suspended particles.

A very suitable liquid for examination with the ultra-microscope is colloidal gold sol which formed the basis of the 'potable gold' of the alchemists, and was rediscovered in 1856 by Faraday, who obtained it by the reduction of gold chloride with phosphorus. The sol can readily be prepared by adding to a very dilute solution of gold chloride, freed from acid by the careful addition of sodium carbonate, a dilute solution of tannin (tannic acid). In the cold, no change occurs, but when the liquid is heated, a pink colour soon begins to develop; and by making further additions of the gold and tannin solutions a clear, deep ruby-red coloured liquid is obtained. This contains the gold in a colloidal state, and is similar, in fact, to ruby glass.

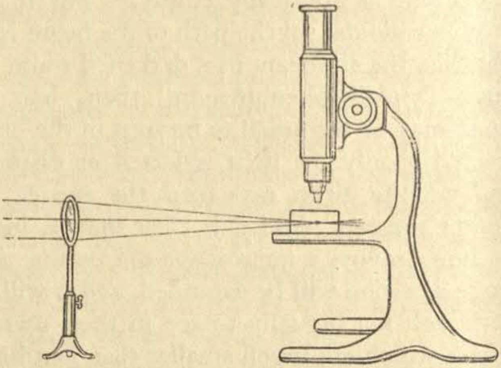


FIG. 21.—ULTRA-MICROSCOPE

A similar colloidal sol can be obtained by passing hydrogen sulphide (sulphuretted hydrogen, H_2S) through a solution of white arsenic (oxide of arsenic). A clear yellow liquid is formed which passes unchanged through filter paper (a finely porous, unglazed paper), and is a colloidal sol of arsenious sulphide.

And how large are those particles which are thus detected in the apparently homogeneous colloidal sols? With the aid of even the most powerful microscope, the smallest particle that can be seen by the ordinary method must have a diameter of not less than about one ten-thousandth part of a millimetre or one two-hundred-and-fifty-thousandth part of an inch; but by means of the ultra-microscope, particles about one-twentieth of this size, with a diameter of about six-millionths of a millimetre ($\frac{6}{1000000}$ mm.) or one four-millionth of an inch, can be detected. This, however, is still about sixty times greater than the diameter of the hydrogen molecule.

From the investigations carried out by means of the ultra-microscope, it is found that colloidal sols may contain particles of very different size, even in the case of the same substance, and there is every reason to believe that there exist, in some at least of the sols, particles which are smaller than can be detected by the ultra-microscope, although they are of greater than molecular dimensions. In short, there appears to be no sharp division between colloidal sols and true solutions, and it is possible to pass gradually and without break from one to the other.

Since matter in the colloidal state is very finely subdivided, the extent of surface exposed is very large relatively to the total volume of the matter. Surface forces, therefore, play an important part and bring about what is known as *adsorption*, or changes of concentration at the surface. Charcoal, a finely porous material with a large surface, has the property (p. 77) of removing noxious gases (*e.g.* sulphuretted hydrogen) from the air and colouring matters from solution. This is due to the fact that under the action of surface forces, the noxious gases or colouring matters are adsorbed or concentrated on the surface of the charcoal. Similarly, gelatinous silicic acid—obtained by adding hydrochloric acid to a solution of water-glass and separating the silicic acid from the sodium chloride by dialysis—when partially dehydrated, forms a porous material, *silica gel.* This also shows the property of adsorption in a very marked degree, and is extensively employed in industry for the recovery of volatile solvents, the removal of gasoline vapour from natural gas, etc. Thus, when air containing the vapour of a solvent such as acetone is passed through a layer of silica gel, the acetone is condensed on the surface of the gel and so removed from the air. The solvent can be recovered by heating the gel.

The readiness with which a substance is adsorbed by a given adsorbent varies with the nature of the substance; and this fact is made use of for the purpose of separating the constituents of a mixture (*e.g.* vitamins (*Chap.* 16) and colouring matters of plants), by an experimental technique known as *chromatography*.

Adsorption plays a very important part in the production and character of colloids. By the adsorption of ions from the dispersion medium or from electrolytes present in solution, the colloid particles acquire an electric charge; and adsorption of the medium as a whole may also take place. In the case of the so-called *suspensoid* colloids, *e.g.* colloidal gold and colloidal arsenious sulphide, the dispersed particles adsorb practically none of the dispersion medium, and their stability is due to their motion (Brownian movement, p. 194), and to the electric charge which they carry. The particles, being charged, mutually repel one another and so agglomeration and precipitation are prevented. In the case of the *emulsoid* colloids, however, *e.g.* gelatin, silicic acid, etc., the dispersion medium itself is adsorbed to a greater or less extent. The greater the adsorption of the medium, the more will the stability and properties of the colloidal sol be dependent on this adsorbed medium, and the less will they depend on the electric charge. Owing to the adsorption of the dispersion medium, emulsoid colloids show certain marked differences in behaviour from that of suspensoid colloids.

That the particles of a suspensoid colloid are electrically charged can readily be demonstrated with a colloidal solution of sulphide of arsenic. If this is placed in a U-shaped tube, and if wires connected with the terminals of a high-voltage battery or dynamo[1] are inserted in the liquid, one in either limb of the tube, it will be found that the sulphide of arsenic migrates towards and collects around the positive terminal. The particles of arsenic sulphide are thus shown to carry a negative charge of electricity. Even with fine suspensions, such as a suspension of fine clay or a slime of peat, the same phenomenon is observed; the clay particles or the peat fibres collect around the positive terminal in a firm mass. Since the effect depends primarily on the voltage of the current, while only an insignificant amount of electricity is used, this process of *electrophoresis*, or electric transport of suspended particles, may be applied for the purpose of freeing a fine suspension from water, and has, in fact, been applied to the drying and purification of clay.

The process of electrophoresis is also applied to the manufacture of articles of rubber. The juice or latex of the rubber plant consists of a liquid in which negatively charged particles of rubber are suspended, and these particles will therefore be carried to the positively charged electrode or anode. Moulds of any desired form, or fabric or wire, may thus be coated with a layer of rubber, and in this way hot-water bottles, bathing caps, etc., may be produced, or wire may be insulated.

---

[1] The ordinary electric-lighting circuit can conveniently be employed, provided it supplies direct current.

Since the stability of the suspensoid colloids is mainly due to the electric charge carried by the particles, precipitation of the colloid is brought about by neutralizing the electric charge. This can be effected by the addition of an electrolyte. Negatively charged colloid particles will preferentially take up or adsorb positive ions, and positively charged colloids will adsorb negative ions, and the charge on the colloid will thereby be neutralized. The colloid particles will then no longer repel one another but will agglomerate into larger particles and settle out of the liquid. Thus, when a small quantity of hydrochloric acid (hydrogen ion) or of calcium chloride (calcium ion) or of some other electrolyte is added to a colloidal sol of arsenious sulphide or of gold, precipitation of the colloid takes place.

A similar behaviour is found in the case of ordinary fine suspensions (*e.g.* of clay in water), the particles of which are also electrically charged; and this fact is sometimes of considerable geological or geographical importance. Thus, the sedimentation of finely divided, water-borne clay is markedly influenced by the purity of the water transporting it, and takes place more rapidly when salts are present than when they are absent. This, indeed, is one reason for the rapid deposition of river mud on mixing with sea-water, and for the consequent silting up of river mouths and the formation of deltas, such as has taken place at the mouth of the Nile and of the Mississippi.

The electrical charge on a colloid particle may be neutralized not only by the ion of an electrolyte but also by another colloid carrying an electric charge of opposite sign. Thus, when a positively charged and a negatively charged colloid, such as ferric hydroxide and arsenious sulphide, are brought together, the oppositely charged particles attract one another, and this leads to a mutual flocculation and precipitation of the colloids.

The process of adsorption plays an important part in the dyeing of textiles. In the case of what are called substantive dyes, the dye itself is in a colloidal state, and may be precipitated and fixed on the fibre by the addition of salts, just as arsenious sulphide is precipitated by electrolytes. In the case of acid and basic dyes one is dealing with coloured ions. Since in an acid bath the textile fibre becomes positively charged, owing to adsorption of hydrogen ion, the fibre will attract and retain negatively charged or acid dyes; but in an alkaline bath the fibre becomes negatively charged and so will attract and retain positive or basic dyes.

Whilst it is found that, in very many cases, silk and wool have the power of taking up and fixing the dye stuff directly, it is frequently found that in the case of cotton the fixation of the dye has to be assisted by a *mordant*, which is either a colloid itself or can give rise to a colloid. The colloid so formed is deposited on and within the fibre to be dyed, and attracts and fixes oppositely charged colloidal dyes. According to the nature of the dye, so must be the nature of the mordant employed. Salts of aluminium, chromium, etc., which give rise to the hydroxides of the metals, are used when the dye has a negative charge or has acid properties (*e.g.* alizarin), while tannic acid and similar substances are employed for dyes with a positive charge or with basic properties. After the dye has been adsorbed, secondary changes may take place which render the dye less easily removed.

In agriculture, also, the colloidal state is of the greatest importance. In the soil there exist various colloidal substances, such as the humus, colloidal ferric hydroxide and aluminium hydroxide, clay, etc. Owing to the presence of these, soluble substances, such as the salts of potassium, phosphates and other substances necessary for the life of the plant, are adsorbed and retained in the soil, and so kept available for the support and nourishment of vegetation instead of being washed away into the rivers and sea. The humus, moreover, being a colloid similar to albumin and gelatin, has the property of imbibing water and so helps to maintain the soil in a moist condition; and it also acts as a substrate for the bacteria concerned in the conversion of nitrogenous organic matter into a form which can be taken up by the plants, as well as for the other bacteria always present in the soil. The water-holding power of the soil colloids may be considerably modified by the addition of various substances, *e.g.* lime; and the addition of lime may have an effect on the fertility of the soil, not only by neutralizing excess of acid but also by altering the structure of the soil colloids.

Owing to the presence of such colloids as ferric hydroxide and aluminium hydroxide, filtration through soil acts as a very efficient means of purifying sewage and other waste water from organic impurities. These impurities in sewage, for example, have been found to be, to a large extent, negatively charged colloids which are therefore precipitated and retained by the positively charged colloids, ferric hydroxide and aluminium hydroxide. By such filtration through the soil, therefore, even the highly impure water which drains from cultivated and manured land is rendered comparatively sweet and harmless. In the same way, the purification of drinking-water by filtration through beds of sand or through charcoal, depends on the removal of impurities by adsorption on the large filtering surface exposed and on the retention of positively charged colloidal matter, bacteria, etc., by the negatively charged sand or charcoal particles.

An important application of the behaviour just described is found in sewage farms, where the drainage of towns is pumped on to the land and the liquid allowed to drain through the porous soil. Here, the waste organic matter as well as phosphates and other salts are retained and afford a rich nutriment for the growing crops, while the liquid effluent which drains away is free from objectionable impurities. By such means can, in suitable surroundings, a source of annoyance and loss be turned to profit.

In the case of emulsoid colloids, such as gelatin, albumin, etc., the stability of the colloid is due not so much to the electric charge on the particles as to the adsorbed water. Such colloids, therefore, are not so sensitive to added electrolytes, and actual precipitation does not take place until the concentration of electrolyte is relatively large, although changes may be brought about in the water-content of the colloid. This comparatively great insensitiveness to electrolytes, further, may be transferred to suspensoids. Thus when gelatin, for example, is added to a colloidal gold sol, the gold is adsorbed by the gelatin and a much greater concentration of electrolyte is required in order to precipitate the gold than is necessary in the absence of the gelatin. The gelatin is said to 'protect' the gold, and owing to this so-called *protective action*, a suspension or suspensoid colloid is rendered much more stable. Indeed, so stable may the colloid become that the colloidal sol may even be evaporated to dryness without destroying the colloidal state; on treating the dried solid with water, it passes back again into the state of a colloidal sol.

In the manufacture of photographic plates, prepared by coating plates with gelatin containing a fine suspension of silver bromide, one finds an important industrial application of the protective action of emulsoid colloids. If a solution of potassium bromide is added to a solution of silver nitrate, silver bromide is formed and separates out as an insoluble curd, quite unsuitable, on account of its coarseness, for photographic purposes. But if gelatin is first dissolved in the solutions of potassium bromide and of silver nitrate, no curdy precipitate but only a uniform colloidal suspension of very fine particles of silver bromide is obtained on mixing the solutions.

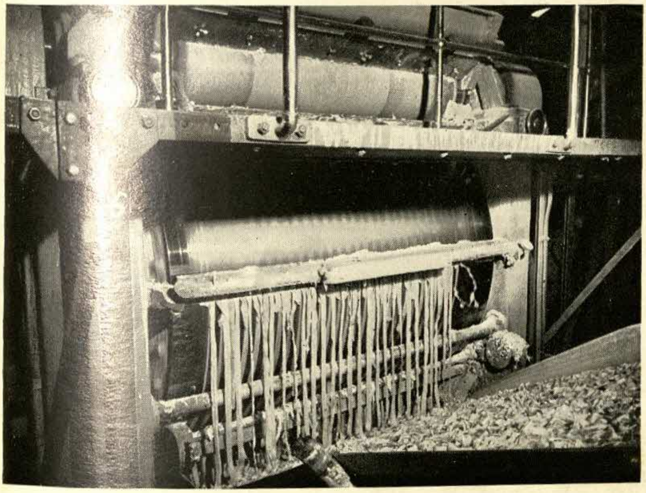
The protective action of emulsoid colloids is also clearly seen in the nature of the curd which is formed from milk, and in the readiness with which it is formed on addition of acid or of rennet. In cow's milk there is a relatively large amount of casein and a relatively small amount of the protective colloid, lact-albumin. Cow's milk, therefore, readily curdles. In human milk, there is a smaller proportion of casein and a larger proportion of lact-albumin. The casein is therefore more effectively 'protected' and curdling takes place less readily. Human milk is, therefore, more readily digested than cow's milk. In ass's milk, the proportion of protective colloid to casein is highest of all, and curdling, therefore, takes place still less readily. The digestibility of ass's milk is greatest of all. By increasing the proportion of protective colloid in cow's milk by the addition, for example, of gelatin, white of egg, or barley water (containing starch), the formation of a curd in the stomach may be more or less completely prevented; and the curd, when formed, is less compact. The digestibility of the milk is thereby increased.

In the manufacture of ice cream, likewise, the addition of protective colloids, like albumin (white of egg) and gelatin, to the milk ensures a smoother product, because the casein is prevented from coagulating and the ice particles are kept very small.

Many colloidal sols, *e.g.* gelatin, starch, etc., when cooled or coagulated, pass into a jelly, owing to the coalescence of the

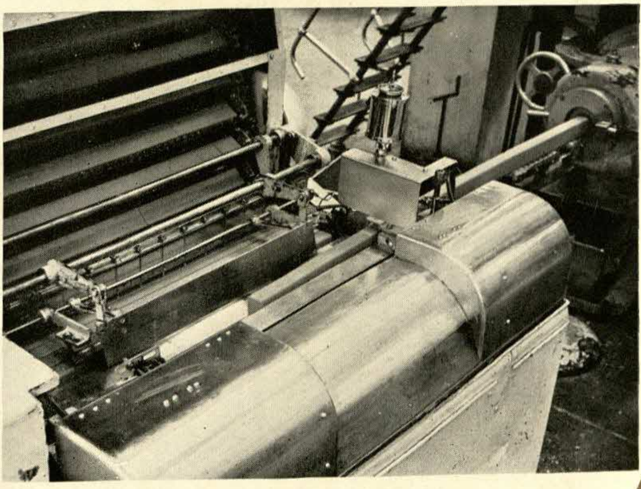
24. MANUFACTURE OF SOAP

Pans in which the saponification is carried out

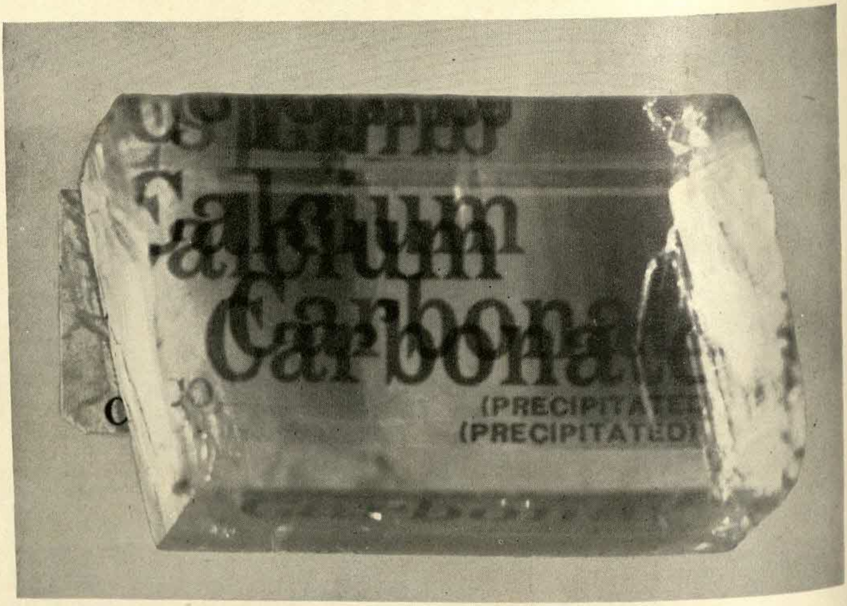


25. RIBBONS OF SOAP BEING SCRAPED OFF CHILLING ROLLER

26. EXTRUSION OF SOAP IN FORM OF BARS



27. LIMESTONE TERRACES, YELLOWSTONE PARK



28. ICELAND SPAR, SHOWING DOUBLE REFRACTION

hydrated colloid particles. The jelly so formed may be regarded as constituted by a honeycomb or network of hydrated colloid, the meshes or cells of which are filled with a dilute solution of the colloid. The water-holding or liquid-holding power of such jellies is sometimes very great, as is seen from the fact that jellies have been obtained which contain less than 0·5 per cent. of the colloid. 'Solidified alcohol,' used as a fuel for spirit lamps, is a jelly formed by colloidal calcium acetate in alcohol.

Although electrolytes, as we have seen, may bring about the precipitation of colloids, they may also, when present in only very small amount, facilitate the dispersion of a solid substance by giving to the particles, by adsorption, the electric charge necessary for the stability of the colloidal sol. This process of deflocculation or breaking up of large particles is spoken of as *peptization*, on account of its superficial resemblance to the process of conversion of insoluble protein into soluble or colloidally dispersed peptone.

Even when adsorbed substances may not, by themselves, be able to peptize solids, they may, by acting as stabilizers and as protective colloids, assist mechanical or other processes in the production of the colloidal state. The production of colloidally dispersed or deflocculated materials by grinding in special mills in presence of protective colloids, or 'dispersators,' is now a considerable industry. Thus, graphite may be obtained in a colloidally dispersed state in water or in oil for use as a lubricant. Very finely divided materials find application, also, in the paint industry and as fillers in paper, rubber, etc.

Although, in recent years, the importance of the colloidal state in its bearing on many of the activities of daily life has become more clearly recognized and more fully appreciated, it is in connection with our conceptions of the constitution of matter that the investigations of microscopic and ultra-microscopic suspensions have gained some of their most brilliant triumphs. For more than two thousand years there has existed in men's minds the idea of matter as made up of separate, discrete particles; and in the nineteenth century, as we have seen, this idea was given a more definite form at the hands of Dalton and of Avogadro. But the particles, the molecules, which make up matter as our eyes reveal it to us, are not in a state of rest. In the case of a gas, these molecules are in a state of almost inconceivable tumult and commotion, which even the restraint imposed by the condensation and the congealing of the gas to the liquid and the solid state is not able wholly to subdue. Such, at least, is the picture of matter which the genius of a Clerk-Maxwell and a Clausius revealed to us in what is known as the kinetic theory of matter. But although this theory has been found to give a satisfactory explanation of the behaviour more especially of gases, and has made it possible to calculate not only the absolute mass of the molecule—the hydrogen molecule weighs about three quadrillionths (or three million million million millionths) of a gram[1]—but also its dimensions (rather less than a three hundred millionth of a centimetre in diameter),[2] and the speed of its flight (say, a mile per second), there were not wanting some who refused to believe in the objective reality of molecules and of the picture presented by the kinetic theory. And yet, even as early as 1827, these molecules, although by their minute size removed far beyond the range of human vision, had, all unknown to their observers, made their presence manifest by the effects which they produced. In that year, the botanist, ROBERT BROWN, while examining suspensions of pollen grains under the microscope, observed that the particles were never at rest, but were in rapid motion, vibrating, rotating, moving irregularly along a zigzag path, sinking, rising—*perpetually* in motion. In this *Brownian movement*, as it is called, the full significance of which has only during the present century been grasped—it had, indeed, been observed long ago by the French naturalist, Buffon, who saw in it a manifestation of life—we have an actual picture of that tumult and commotion of the molecules which were revealed to the mental vision of mathematical physicists. But it is not, of course, the motions of the molecules themselves that one sees in the Brownian movement, but only the effect of the incessant bombardment of the coarser, visible particles of the suspension, by the molecules of the liquid.

Over a lengthened period of time, the number of blows which a suspended particle of sufficient size, say such as is visible to the naked eye, would receive from the molecules of the liquid in which it is suspended, would be the same in the different directions. The suspended particle, therefore, would show no sign of motion. But if the period of time is made sufficiently short, the number of impacts of the liquid molecules will no longer be equal in different directions, the impacts will no longer balance one another, and if the suspended particle is small enough it will, at each blow, be caused to move, first in one direction and then in another, and all the faster the smaller the particle; and it is this motion of a particle of a suspension under the blows which are rained upon it by the molecules of the liquid, that constitutes the Brownian movement. With particles of ultra-microscopic dimensions the phenomenon is exhibited with extraordinary vividness, and it is an impressive sight to observe the rapid darting motions of a colloid particle by means of the ultra-microscope. As Zsigmondy, who first observed it, wrote: 'A swarm of dancing gnats in a sunbeam will give one an idea of the motion of the gold particles in the hydrosol of gold. They hop, dance, spring, dash together and fly apart so rapidly that the eye can scarcely make out their movements. . . . These motions show that there is a continual mixing together of the interior parts of every liquid going on unceasingly, year in year out.' It is to this Brownian movement that the stability of colloidal sols is largely due. From the careful quantitative investigations of this phenomenon, carried out during the present century, the various molecular magnitudes—the kinetic energy of the particles and their velocity of diffusion, for example—have been computed; and such is the closeness of agreement between the results so obtained and the values which the kinetic theory would lead one to expect, that one cannot any longer hesitate to believe that in the rapid, darting motions of the ultra-microscopic particles there is made manifest to us something of the turbulent stir and bustle which is going on unceasingly in that underworld of molecules which lies beyond the reach of our senses.

---

[1] This number is more conveniently represented by 3×10^{-24} gram, which is the same as dividing 3 by 10 twenty-four times in succession.

[2] The diameter of a hydrogen molecule is $2{\cdot}40 \times 10^{-8}$ cm.

Chapter 12

MOLECULAR ARCHITECTURE

Of all the known elements, the element carbon, familiar to all in the three physically distinct forms, charcoal, graphite, diamond, stands out pre-eminent in its power of forming compounds with other elements. So numerous, indeed, are its compounds—about 700,000 and rapidly increasing in number—that their study has developed into a special branch of chemistry, *organic chemistry*. This name is a survival from an older period when chemists drew a distinction between the compounds occurring in the non-living, mineral world, and those occurring in the living animal and plant organisms, and which were thought to be producible only with the help of a special form of energy, the so-called vital force, inherent in the living cell.

In 1828, however, the German chemist, Friedrich Wöhler, obtained the compound urea, $NH_2{\cdot}CO{\cdot}NH_2$, known until then only as a product of animal metabolism, by heating the salt ammonium cyanate, NH_4OCN, a compound which can be prepared from non-living, mineral materials. The view, therefore, that any essential difference exists between the two classes of compounds, or that the chemical laws which obtain within the domain of living nature are different from those which are found in inanimate nature, can no longer be held. Not only can many, very many, of the compounds which were formerly regarded as typical products of animal and vegetable metabolism, typical organic compounds in the older sense, be prepared in the laboratory from purely mineral materials, but the synthetic production of not a few of these compounds has even developed into industries of enormous magnitude. The term 'organic chemistry' is still retained, not with its old signification, but merely as denoting the chemistry of carbon and its compounds; for, indeed, the vast majority of these 'organic' compounds are found in no animal or plant organism, but have been prepared by the intelligent combining together of substances by the chemist.

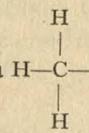
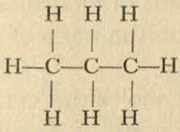
I have referred here particularly to the compounds of carbon not with the intention of describing either the methods of preparation or the specific properties of any of these substances, but rather for the purpose of discussing briefly what may be called *molecular architecture*, or the arrangement of the atoms, within the molecule. This I wish to do with special reference to a phenomenon which, although met with in the case of the compounds of other elements, is found with extraordinary frequency in the case of the compounds of carbon. This is the phenomenon to which the name of *isomerism* was given, and of which an early example was furnished by ammonium cyanate and urea.

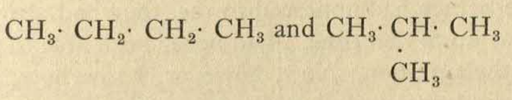
When Dalton introduced his atomic theory, the basis on which all modern chemistry has been built, he showed, as we have seen, that a compound could be regarded as being formed by the combination or uniting of the atoms of the constituent elements in certain constant and definite proportions. But while the law, 'One compound, one composition,' has remained unshaken, the progress, more especially, of organic chemistry soon showed that the converse statement, 'One composition, one compound,' which, to the earlier chemists, was equally an article of faith with the former, is very far removed from the truth.

It has already been pointed out (p. 15) that the constituent atoms of a compound are linked together so as to form a definite molecular pattern, and as the number of compounds of carbon became multiplied it began to be more and more frequently observed that the same elements may be united in the same proportions to form compounds with entirely different properties. More than a hundred different compounds, for example, can be produced by combining together nine atoms of carbon, ten atoms of hydrogen, and three atoms of oxygen. To this phenomenon, that different compounds may have the same composition, the term *isomerism* was applied. Just as the same set of bricks can, by varying their arrangement, be formed into structures of totally different kinds, so also the same atoms can, by varying their arrangement within the molecule, give rise to different molecular structures, or different compounds. In other words, the discovery of isomerism, so entirely unforeseen by Dalton and by the earlier organic chemists, led to the recognition of the fact that the properties of a compound depend not merely on its composition, but also on its internal structure or the arrangement of the atoms within the molecule; and our knowledge of a substance is not complete until we know what is the internal structure or *constitution* of the molecule. We must gain a knowledge of molecular architecture. A knowledge of the molecular constitution is, moreover, essential for the successful building up or *synthesis* of a compound from simpler materials, which will be discussed more fully in the following chapters.

To elucidate the constitution of the different naturally occurring compounds of carbon is one of the main aims of the organic chemist, and in the case of the more complex compounds, the problem becomes one of the greatest difficulty. As to how this problem is solved, only this much can be said here. Through the laborious efforts of numberless chemists, a knowledge has been gradually built up of the internal structure or constitution of a very large number of substances, and also of the relations between these different structures and the physical and chemical properties of the compound. In order to determine the constitution of an unknown compound, therefore, the properties and reactions of the substance are studied, and the compound is also, by the action of various chemical reagents, decomposed into simpler compounds. It is broken down into bits, as it were, and one then seeks to identify the fragments, the simpler substances, so obtained, with substances of which the constitution is already known. From the knowledge gained in this way, the chemist, with his imaginative insight and wide knowledge of how substances react with one another, then attempts to piece the fragments together again, and so to build up or synthesize the original substance.

The task of elucidating the constitution of organic compounds, however, would be a hopeless one without the aid of some guiding principle and some method by which the molecular constitution can be represented. It was, therefore, a great step forward when the Scottish chemist, ARCHIBALD SCOTT COUPER, and the German chemist, FRIEDRICH AUGUST KEKULÉ, in 1858, showed how molecular constitutions could be represented diagrammatically, and the relations between different compounds made readily intelligible, by using as guiding principles the quadrivalency of the carbon atom (p. 15) and the capacity of carbon atoms for mutual linking.

Although there is, of course, no material link or bond between the atoms, one can nevertheless represent union between atoms as if it were material by means of a line or lines (dot or dots), according to the valency of the atom (p. 16). Thus, as we have already seen, we can represent the compound methane by the diagrammatic or *graphic* formula  $\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—H} \\ | \\ \mathrm{H} \end{array}$, and the higher hydrocarbons of that series by such a chain of carbon and hydrogen atoms as  $\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} \\ & & | & & | & & | \\ \mathrm{H} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C—H} \\ & & | & & | & & | \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} \end{array}$; a formula which can also be written in the simpler form, $CH_3{\cdot}CH_2{\cdot}CH_3$, known as a *constitutional* or *structural formula.*[1] Using valency as a guiding principle, moreover, it is possible not only to represent the molecular constitution of known compounds, but also to foresee the possible existence of isomeric compounds. Thus, in the hydrocarbon propane, C_3H_8, the only possible arrangement of the atoms is that shown in the formula, $CH_3{\cdot}\ CH_2{\cdot}\ CH_3$; whereas for butane, C_4H_{10}, two arrangements are possible:



$$CH_3{\cdot}\ CH_2{\cdot}\ CH_2{\cdot}\ CH_3 \text{ and } \begin{array}{c} CH_3{\cdot}\ CH{\cdot}\ CH_3 \\ \cdot \\ CH_3 \end{array}$$

Two isomeric butanes (normal butane and isobutane) are possible and are known. In the former compound one has what is called a *straight chain*, and in the latter compound a *branched chain*.

As the number of carbon atoms increases the possible number of isomers increases more rapidly, so that one can have three pentanes (C_5H_{12}), five hexanes (C_6H_{14}), nine heptanes (C_7H_{16}), eighteen octanes (C_8H_{18}), etc.

---

[1] Such formulæ show how the atoms are linked without the insertion of each individual bond.

Further, it can be seen that by replacing one atom of hydrogen in propane, $CH_3{\cdot}CH_2{\cdot}CH_3$, by one atom of, say, chlorine, two isomeric chlorides can be obtained, represented by the formulæ $CH_3{\cdot}CH_2{\cdot}CH_2Cl$ and $CH_3{\cdot}CHCl{\cdot}CH_3$. These two and only these two chlorides are known.

In the compounds mentioned, namely, saturated hydrocarbons (p. 53) and derivatives of these, the carbon atoms are linked by only one valency bond. In unsaturated compounds (p. 53), however, two carbon atoms may be linked by two or by three bonds, *e.g.* $CH_2{:}CH{\cdot}CH_3$ (propylene) and $CH{\vdots}CH$ (acetylene).

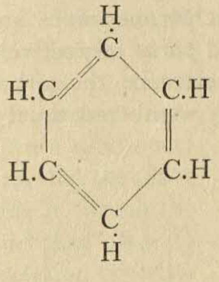
The compounds just considered represent comparatively simple molecular structures, but other more complex arrangements of atoms, including atoms of elements other than carbon, may be similarly formulated on the basis of the Couper-Kekulé theory of molecular structure.

The origin of the theory of molecular constitution as it arose in the artistic and imaginative mind of Kekulé, who had entered the University of Giessen as a student of architecture, has been recounted by Kekulé himself. During a period of residence in London he was returning from a visit paid at Islington to where he was staying at Clapham. 'One fine summer evening,' he relates,[1] 'I was returning by the last omnibus, "outside" as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie, and lo! the atoms were gambolling before my eyes. Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time, I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain.' And then he adds: 'I spent part of the night putting on paper at least sketches of these dream-forms.' From these sketches were developed the *constitutional* or *structural* formulæ, of which examples have been given above.

And again he had a dream. Now he was in Ghent, and dozed before his fire. Again he saw the atoms gambolling before his eyes, the chains twining and twisting in snakelike motion. 'But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke'; but the picture Kekulé had seen of the snake which had seized its own tail gave him the clue to one of the most puzzling molecular structures, the structure of the benzene molecule, a ring of six carbon atoms to each of which one hydrogen atom is attached. Thus we obtain the graphic formula[1] of the benzene molecule,

---

[1] F. R. Japp, 'Kekulé Memorial Lecture' (*Transactions of the Chemical Society*, 1898).



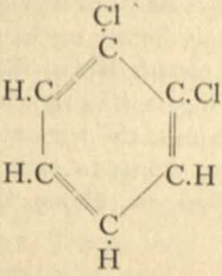
the 'ring' of carbon atoms being written in the form of a hexagon[2] instead of in the form of a circle. 'Let us learn to dream,' said Kekulé, 'then perhaps we shall find the truth.' 'But,' he wisely added, 'let us beware of publishing our dreams before they have been put to the proof by the waking understanding.' The hexagonal form of the benzene molecule has been confirmed by X-ray examination, as have, indeed, many of the other complex molecular structures devised by chemists.

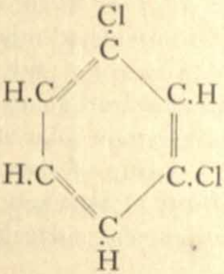
The hexagonal ring structure accepted for the molecule of benzene introduces possibilities of isomerism which do not exist in the open-chain compounds previously considered. Thus, if two atoms of hydrogen are replaced by, say, two atoms of chlorine, three isomeric compounds can be formed, as shown by the formulæ:

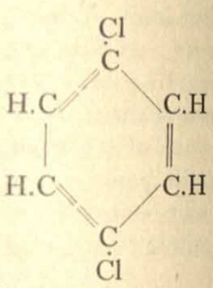
---

[1] Just as in the study of the architecture of buildings, plans and architectural drawings are necessary for the proper understanding of the subject, so also structural formulæ are required for the understanding of molecular architecture. They are required for understanding, not necessarily for memorization.

[2] The reason why six carbon atoms readily arrange themselves in the form of a hexagon is that the four valencies of a carbon atom are directed in space towards the four corners of a regular tetrahedron (p. 208). The angle between the valencies is 109° 28′, and the angles of a hexagon are 120°. The six carbon atoms can thus join up to form a hexagon with only a small degree of 'strain.'

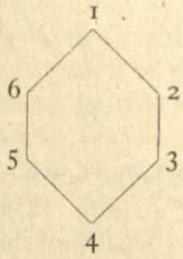






The three isomeric dichlorobenzenes are distinguished by the terms *ortho-*, *meta-* and *para-* respectively.

For convenience of reference, the carbon atoms of the benzene ring are also frequently numbered thus:



The three isomeric dichlorobenzenes may, therefore, also be named, 1:2–, 1:3– and 1:4–dichlorobenzene respectively.

If two hydrogen atoms in the benzene ring are replaced by the group CH_3–, one obtains three isomeric *xylenes*, known as ortho-, meta- and para-xylene. Terephthalic acid ($HOOC{\cdot}C_6H_4{\cdot}COOH$), used in the production of the synthetic fibre terylene (*Chap.* 14), is produced from para-xylene, derived from petroleum.

The conception of closed rings of carbon atoms has shown itself capable of an almost limitless development so as to include compounds with rings of atoms varying both in number and in nature.

By the introduction of the doctrine of valency and of Couper's and Kekulé's diagrammatic method of representing molecular constitution, a satisfactory basis seemed to have been obtained for the future development of organic chemistry. And yet, it was not long before the inadequacy of this theory of chemical structure became only too apparent, owing to the discovery that, in some cases, the number of isomeric compounds is greater than can be represented by the structural formulæ of Couper and Kekulé. A new isomerism was discovered, an isomerism which manifested itself in the property known as *optical activity*. Let me try to explain this.

Early last century it was discovered that when a ray of light is passed through a crystal of Iceland spar, the electromagnetic vibrations, which propagate the light, andwhich, ordinarily, take place in all directions at right angles to the path of the ray, are all brought into one plane. The light is said to be *polarized*. When, now, this polarized light is passed through certain substances, quartz, turpentine, a solution of cane sugar, etc., it is found that the plane of polarization, the plane in which the electromagnetic vibrations take place, is rotated or twisted, this rotation or twisting taking place sometimes to the right, sometimes to the left; an effect which one can illustrate by the twisting of a strip of stout paper into a right-handed or left-handed spiral, as represented in Fig. 22. Substances which possess this property of rotating the plane of polarized light are said to be 'optically active.'

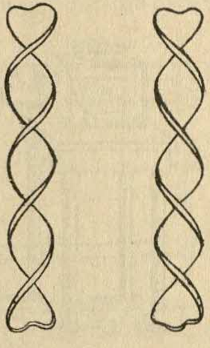


FIG. 22.—RIGHT- AND LEFT-HANDED SPIRALS

This property of optical activity can also be demonstrated by a modification of a very interesting experiment due to Sir GEORGE STOKES. When a parallel beam of light from a projection lantern (Fig. 23) is reflected vertically downwards by means of a mirror, through a column of water rendered slightly turbid by the addition of a few drops of an alcoholic solution of rosin, the path of the beam is rendered visible by the fine suspension of rosin particles (Tyndall phenomenon, p. 184); and the beam of light appears equally bright all round. But if the light from the lantern is first polarized by passage through a so-called Nicol prism formed from Iceland spar, or through a disc of *polaroid*,[1] and is then reflected downwards through the column of water, the appearance obtained is that of a band which is light *only on two* opposed sides, and dark on the other two opposed sides. On rotating the Nicol prism or polarizing disc, the band also rotates and turns alternately its light and dark sides to the eye. The effect produced is as if the beam of light on passing through the Nicol prism or polaroid disc, were given a flat form, like a book, from the two opposite edges of which light is emitted,

---

[1] Polaroid consists of a film of cellulose acetate mounted between two plane glass plates. The film is a matrix for sub-microscopic dichroic crystals accurately oriented in such a way that the entire film acts as a single polarizing crystal.

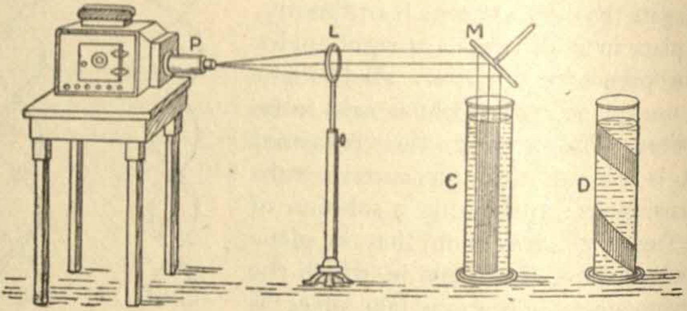


FIG. 23.—DEMONSTRATION OF THE POLARIZATION OF LIGHT

Light from a lantern is polarized by passage through the polarizing prism P, and the beam of light is then directed by the lens L on to a mirror M, by which the light is directed vertically downwards through water contained in the cylinder C, and rendered turbid by a fine suspension of rosin. A vertical, polarized band of light is obtained. If the cylinder C is replaced by D, which contains a concentrated solution of cane sugar, the band of light is twisted into the form of a spiral.

while the sides remain dark. Thus we have illustrated the phenomenon of polarization of light. If, now, the cylinder of water is replaced by a cylinder containing a solution of cane sugar and a suspension of rosin, the band of light is twisted into a spiral form; and on rotating the polarizing prism or disc, this spiral band of light appears to move with a screw-like motion. From the fact that the different rays of coloured light which together constitute white light are twisted or rotated to different extents (the blue rays being rotated more than the red), the spiral band of light shows the colours of the rainbow.

What then is the explanation to be given of this remarkable property of substances, the study of which, starting with the brilliant discoveries of PASTEUR[1] in 1848, has occupied the attention of many of our foremost chemists down to the present day? (Plate 31.)

When Pasteur commenced the investigations which were to initiate a revolution in the current ideas regarding the molecular structure of organic compounds, two isomeric acids were known having the same composition, namely, tartaric acid and paratartaric acid (now called racemic acid). The former, which is found occurring in grape juice, is optically active; the latter is inactive. On examining the crystals of these two acids, and of a number of their salts, Pasteur found that whereas the crystalline faces of the inactive racemic acid and its salts were all fully developed, and the crystals symmetrical (Fig. 24), the full development of the crystalline faces of the optically active tartaric acid was interrupted by the occurrence of so-called hemihedral faces (Fig. 24). The occurrence of these hemihedral faces was regarded by Pasteur as the outward and visible manifestation of the property of optical activity, in accordance with a view which had been suggested by Sir JOHN HERSCHEL in the case of crystalline quartz, which is also optically active. But whereas quartz is optically active only in the crystalline state, tartaric acid retains the property even when dissolved. In the former case, the property depends on the crystalline structure; in the latter, it depends on the internal molecular structure.

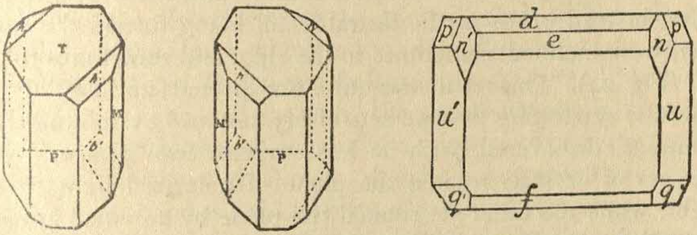


FIG. 24.—HEMIHEDRAL CRYSTALS OF *d*- AND *l*-SODIUM AMMONIUM TARTRATE, AND HOLOHEDRAL CRYSTAL (RIGHT) OF SODIUM AMMONIUM RACEMATE

---

[1] Louis Pasteur, the son of a tanner, was born in 1822. For a number of years he was Professor of Chemistry at Strasbourg, Lille, and Paris, and carried out a large number of important investigations in biochemistry and bacteriology. On his work, antiseptic surgery was built up and a cure for rabies or hydrophobia obtained. He died in 1895.

A further discovery was made by Pasteur. During his investigation of one of the salts of tartaric and racemic acid (namely, sodium ammonium tartrate and sodium ammonium racemate), Pasteur found, as was to be expected, that the crystals of the tartrate resembled those of the other tartrates he had examined in possessing hemihedral faces, arranged in a similar manner in the different crystals. The crystals obtained by crystallization from a solution of the racemate, however, instead of being holohedral, with the crystalline faces fully developed, were found also to have hemihedral faces; but these hemihedral faces, instead of, as in the tartrates, all being turned the same way, were inclined, sometimes to the right and sometimes to the left (Fig. 24). This result was quite unexpected; and Pasteur, on carefully separating the two sets of crystals and examining their solutions, discovered, with no less surprise than pleasure, that one set of crystals rotated the plane of polarized light to the right, while the other set rotated the plane by an equal amount to the left. On dissolving together equal amounts of the two sets of crystals, a solution was obtained which was optically inactive.

Here, then, we have the discovery of that new kind of isomerism to which reference has just been made, and which showed the inadequacy of the structural formulæ of Kekulé. The two salts into which the racemate had been separated were identical in all their chemical and physical properties, save only in the disposition, to the right or to the left, of the small hemihedral faces occurring on their crystals, and in the property of rotating the plane of polarized light to an equal extent but in opposite directions. From these two salts, Pasteur obtained two different tartaric acids; one having the power of rotating the plane of polarized light to the right and identical with the acid occurring in grape juice, the other hitherto unknown and having the power of rotating the plane of polarized light to the left. Moreover, on mixing together in solution equal quantities of these two optically active acids, there separate from the solution crystals of the inactive racemic acid, which is thus shown to be a compound of the two active acids in equal proportion.

The discovery of the two optically active tartaric acids was a momentous one, effecting a revolution in the views of chemists regarding molecular structure; and one can well understand the feeling of happiness and the nervous excitement by which Pasteur was overcome on making the discovery. Rushing from his laboratory and meeting the *préparateur* in physics, he embraced him, exclaiming: 'I have just made a great discovery! I have separated the sodium ammonium paratartrate into two salts of opposite action on the plane of polarization of light. The dextro-salt is in all respects identical with the dextrotartrate. I am so happy and overcome by such nervous excitement that I am unable to place my eye again to the polarization apparatus.' The question, however, now arose as to how the existence of the two optically active tartaric acids could be explained.

All material things belong to one or other of two classes, according as the image which is formed of the object in a mirror is such that it can or can not be superposed on the object. In the case of a cube, for example, the image formed in a mirror is identical with the object, and one can imagine the image superposed on the original cube. A cube is a symmetrical object. But if a right hand is held in front of a mirror, the image which is obtained represents a left hand, and this cannot be superposed on the right hand; a right hand will not fit into a left-hand glove. A hand, therefore, is an asymmetrical object, which can exist in two distinct, so-called *enantiomorphic* forms, similar in all respects, but not superposable, not identical. And when one examines the crystals of the two optically active tartaric acids (or of their salts), it is seen that they also are related to each other as the right hand is to the left hand; each represents the non-superposable mirror image of the other (Fig. 24), and the two crystals, although in all points similar, are not identical. If, however, the crystalline form is to be regarded, as Pasteur regarded it, as a visible manifestation of the internal structure, one is led to the conclusion that the *molecular* structures of the two active tartaric acids are asymmetric and enantiomorphously related to each other as object to non-superposable mirror image. 'Are the atoms,' Pasteur asked, 'are the atoms of the dextro-acid grouped in the form of a right-handed helix, or do they stand at the corners of an irregular tetrahedron, or are they arranged in some other asymmetrical manner?' And he replied, 'We are not as yet in a position to answer these questions. But it cannot be a subject of doubt that there exists an arrangement of the atoms in an asymmetric order, having a non-superposable image.'

Looking back on the experimental investigations of Pasteur, one cannot suppress a feeling of disappointment that it was not vouchsafed to him, with the clear views he possessed, to take but a little step forward and to develop these views into a theory of molecular structure. But the time was not yet ripe, and it was not until after more than twenty years that the study of organic chemistry furnished a sufficient number of examples of optically active compounds to make it possible to give an answer to Pasteur's questions. Nevertheless, Pasteur introduced into chemistry a conception of extraordinary importance and fruitfulness, the conception of *molecular asymmetry*, and he recognized that molecular structure is not a matter of two dimensions only, but of three. The atoms are not arranged in a plane, as the formulæ of Couper and of Kekulé represent them, but in three-dimensional space. In this way Pasteur inaugurated a new chemistry, a 'Chemistry in Space' or 'Stereochemistry.'

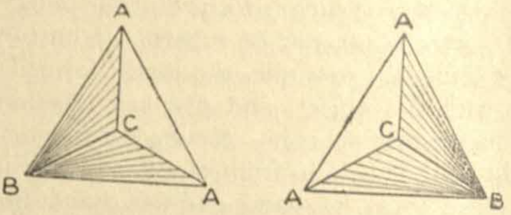


Fig. 25

The conception of molecular asymmetry and the idea of the grouping of the atoms at the corners of an irregular tetrahedron were developed, in 1874, into a consistent theory of molecular structure, embracing the optically active isomeric compounds, by a Dutch and a French chemist independently, van't Hoff and Le Bel.

If we imagine a carbon atom at the centre of a tetrahedron, and if the four atoms or groups, with which, as we have seen, a carbon atom can be united, are situated at the four corners of the tetrahedron, it will be found that so long as two, at least, of the atoms or groups are the same, the molecule, represented as a tetrahedron, will be symmetrical and its mirror image will be superposable on and therefore identical with the original. This will be clear from an inspection of Fig. 25, which represents such a tetrahedron and its mirror image. The right-hand tetrahedron, obviously, only requires to be turned through an angle of rather more than 90°, on the corner B as a pivot, to become identical in disposition with the left-hand tetrahedron.

If, however, the four atoms or groups attached to the carbon atom are all different, the molecule, as represented by the tetrahedron, becomes asymmetric, and gives a mirror image which is no longer superposable on the original. Two isomeric forms are therefore possible. This will be understood from Fig. 26. Viewing these tetrahedra from a similar position, we see that the groups B C D, in the one case, are arranged from left to right (clockwise); in the other case, from right to left (counter-clockwise). If one of these represents a molecule which rotates the plane of polarized light to the right, the other will represent a molecule which rotates the plane of polarized light to the left.

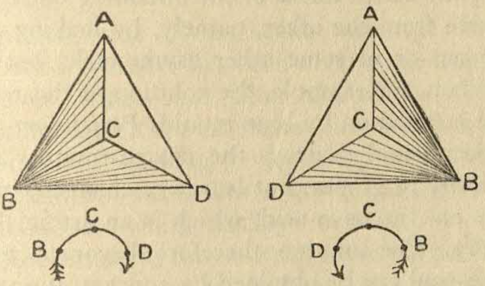


FIG. 26

The views of van't Hoff and Le Bel have received the amplest confirmation. Not only has it been found that the molecules of all compounds which are optically active do contain at least one atom of carbon to which four different atoms or groups are attached—a so-called *asymmetric carbon atom*—or are, for some other reason, asymmetric, but also, no compound has been obtained the possible existence of which could not be predicted by means of the van't Hoff and Le Bel theory. So fruitful has the conception of molecular asymmetry and of the asymmetric carbon atom proved, that it has been extended also to the atoms of elements other than carbon, of which optically active isomers have been prepared.

We have already seen that in the case of tartaric acid—and the same holds for all other optically active substances—there exist, or can exist, not only the two optically active isomers, but also an inactive isomer, produced by the combination of the two oppositely active forms in equal amounts, and separable again, by suitable means, into the active forms. This inactive form is known as the *racemic* form. In the case of one particular salt, sodium ammonium paratartrate, as we have seen, this breaking up of the racemic form (the paratartrate) takes place on crystallizing from water at the ordinary temperature. But this method is capable of only a limited application. Pasteur, however, introduced two other methods for effecting the resolution of the racemic into the active forms or for obtaining one of the active forms separate from the other, namely, by making use of some living organism or of some other asymmetric, optically active material. When, for example, the solution of the racemic paratartaric acid is acted on by blue mould, *Penicillium glaucum*, the fungus feeds on and destroys the dextro-rotatory acid, which occurs naturally in grapes, but leaves unchanged, or acts much more slowly on, the lævo-acid, which is an artificial product of the laboratory. The solution, therefore, becomes lævo-rotatory, and the lævo-acid can be obtained by concentrating the solution and allowing it to crystallize. In the process of fermentation, also, under the action of various enzymes, which are themselves asymmetric agents, produced in living animal and plant cells, we find a similar selective action. Thus, whereas the naturally occurring dextro-rotating glucose, the well-known grape sugar, undergoes fermentation, the lævo-rotating glucose, a compound obtained only artificially, remains unchanged in the presence of yeast. An asymmetric agent acts only on materials of similar asymmetry to itself, just as a right-handed screw will fit only into a right-handed thread. *So long as the two optically active isomers are brought into relations with symmetrical agents, they behave identically; but when they react with an asymmetric agent, a different behaviour is exhibited by the two forms.*

This selective action is of great physiological importance, since in all life processes, such as digestion and assimilation, one is dealing with the action of the optically active, asymmetric materials contained in the cells and tissues. It is found, therefore, that although the naturally occurring albumins and sugars, for example, are capable of being digested, the isomeric compounds of opposite activity pass through the body without being absorbed. And a similar differentiation of action is met with in the case of many of the optically active alkaloids. 'Here, then,' said Pasteur, 'the molecular asymmetry proper to organic substances intervenes in a phenomenon of a physiological kind, and it intervenes in the role of a modifier of chemical affinity. . . . Thus we find introduced into physiological principles the idea of the influence of the molecular asymmetry of natural organic products, of this great character which establishes, perhaps, the only well-marked line of demarcation that can at present be drawn between the chemistry of dead matter and the chemistry of living matter.'

In the investigation of molecular structure, the study of optically active substances has been of supreme importance, and the knowledge which has been gained has exercised an important influence on the understanding and interpretation of biological processes, opening to physiology, as Pasteur said, new horizons, distant but sure. But it is not merely the domain of the physical sciences which has been enriched by the investigations of stereochemistry; the most fundamental problems of life, our very ideas with regard to life itself, and the phenomena of life, receive illumination.

Until 1828, as we have seen, the production of the organic substances occurring in the animal and vegetable organisms was considered to be the prerogative of life; but the synthetic production in the laboratory of many of the compounds which are typical products of the animal and vegetable organism led to the abandonment of that belief, and science began to look upon the phenomena of life as completely explicable in terms of physics and of chemistry. But the discovery and investigation of optically active compounds introduced a new factor. As Professor F. R. Japp, in his Presidential Address to the Chemical Section of the British Association in 1898, so admirably emphasized, 'the phenomena of stereochemistry support the doctrine of vitalism as revived by the younger physiologists, and point to the existence of a directive force which enters upon the scene with life itself, and which, whilst in no way violating the laws of the kinetics of atoms, determines the course of their operation within the living organism.'

In Nature, most asymmetric compounds are found occurring in *one* of the optically active forms only. Dextro-rotatory tartaric acid, for example, occurs in grape juice, but the lævo-rotatory acid is not found in Nature, and is known only as a laboratory product; grape sugar likewise occurs naturally only as the dextro-rotatory form; while the albumins are lævo-rotatory. When, however, it is attempted to prepare an asymmetric compound in the laboratory from symmetric substances only, from substances, that is to say, which are not themselves optically active, it is always found that the product obtained is *inactive*. As Pasteur said: 'Artificial products have no molecular asymmetry; and I could not point out the existence of any more profound distinction between the products formed under the influence of life and all others.'

It is true that the inactive, racemic form, which is obtained as the result of artificial synthesis, can be separated into the two optically active forms, with the help of asymmetric, optically active compounds; or one can even, by the process of fermentation or the action of organisms, destroy one of the active forms and so obtain a single optically active compound. But these processes involve the use either of living organisms or of materials which have been produced by living organisms, and the production of the active form is, therefore, due directly or indirectly to living matter. However, as has been pointed out, Pasteur found that, in some cases, the resolution of the racemic form can be effected simply by crystallization. By allowing a solution of the inactive racemic sodium ammonium paratartrate to crystallize, crystals of the dextro- and of the lævo-rotatory sodium ammonium tartrate were deposited separately, and could, owing to the difference in their crystalline forms, be distinguished from one another and be separated by hand. Since the original racemic paratartrate could be prepared synthetically from symmetrical materials by the action of only symmetrically acting reagents, and since this racemic form could be resolved into the active forms by the symmetrically acting process of crystallization, it was thought that 'the barrier which M. Pasteur had placed between natural and artificial products' had been thereby broken down. And this was undoubtedly the view held by the majority of chemists.

But was this view correct? Pasteur certainly did not think so, and he pointed out very pertinently that 'to transform one inactive compound into another inactive compound which has the power of resolving itself simultaneously into a right-handed compound and its opposite, is in no way comparable with the possibility of transforming an inactive compound into a *single active* compound. This is what no one has ever done; it is, on the other hand, what living nature is doing unceasingly before our eyes.' The artificial, racemic compound, certainly, had been resolved into the two active forms by the symmetrical process of crystallization, but these two forms had not been *separated* from each other; both active forms were present side by side. Their separation 'requires the living operator, whose intellect embraces the conception of opposite forms of symmetry.' And, as Professor CRUM BROWN asked long ago: 'Is not the observation and deliberate choice by which a human being picks out the two kinds of crystals and places each in a vessel by itself, the specific act of a living organism of a kind not altogether dissimilar to the selection made by *Penicillium glaucum*?' (a mould which, as we saw, destroys one optically active form but not the other).

While Pasteur certainly believed that all the attempts which had been made to synthesize a single optically active form, without the intervention, direct or indirect, of life, had been unsuccessful, he appears to have held the view that as science advanced, the inability to effect such a synthesis might be removed; for while he recognized the necessity for the existence of asymmetric forces 'at the moment of the elaboration of natural organic products,' he conceived the possibility that such asymmetric forces might lie outside the living organism and 'reside in light, in electricity, in magnetism, or in heat.' In 1894, also, van't Hoff made the suggestion that the formation of optically active compounds might take place under the directive action of right or left circularly polarized light. Many attempts were made to effect the synthesis of such compounds under the action of circularly polarized light, but it was not till 1929 that success was attained. By the action of circularly polarized light on a symmetrical compound, an optically active compound was obtained, the rotatory power of which varied in sign according as the light was dextro- or lævo-circularly polarized. The possibility of an asymmetric synthesis under the directive action of a purely physical force was thereby demonstrated. Moreover, it has been shown that dextro-circularly polarized light predominates at the earth's surface in reflected sunlight, and it would therefore appear that an unsymmetrical form of photochemical energy exists in Nature under the directive action of which an asymmetric synthesis could take place. The possibility that the formation of the first asymmetric molecule (from which other asymmetric molecules might later be formed) took place under such directive influence has thus been established. The proof that it did in fact so take place cannot of course be given.

Chapter 13

DYES, PERFUMES, DRUGS AND INSECTICIDES

It may, perhaps, have seemed to some that however interesting, as an intellectual speculation, the theories of molecular structure discussed in the previous chapter might be, however much they might satisfy a philosophical curiosity regarding the mystery which lies at the heart of things, they could be of very little practical importance and could scarcely come at all into direct touch with the daily life of mankind. Nothing could be farther from the truth. Kekulé's dreams, perhaps, were an interesting psychological phenomenon, but the stuff that his dreams were made of, the theories of molecular structure, were as important for the advance and development of organic chemistry as a chart and compass are for a mariner. For, it must be remembered, the purpose of a scientific theory is not only to explain or co-ordinate knowledge already acquired, but also to be a guide to the exploration of the unknown.

When Kekulé saw in his dreams the dancing atoms range themselves in chains and loop themselves into rings, and when he evolved from these dream-forms his theory of molecular structure, he not only enabled chemists to interpret the relations between compounds already known, but he guided them also to the discovery and preparation of a multitude of new compounds or new molecular structures. He was, moreover, all unwittingly no doubt, laying the basis and foundation of some of the greatest industries of the present day. Without his theory of molecular structure, supplemented by the stereochemical theory of van't Hoff and Le Bel, there could not have been built up that vast structure of organic chemistry such as we know it at the present day, nor could we have witnessed that crowning achievement of chemists, the artificial, synthetic preparation of many of Nature's own products, and the industrial production of those innumerable dyes, therapeutic agents, perfumes and other materials which are regarded as necessaries in our modern civilization.

While, however, the theories of molecular structure and constitution gave the guidance necessary for the altogether phenomenal development of organic chemistry during the past hundred years, that development could actually take place only through the genius, scientific insight, energy and persistence of hundreds of zealous workers who devoted themselves to the development of knowledge by experimental investigation, and to the task of elucidating the constitution of and synthesizing thousands of organic compounds. And it must not be forgotten that the industries dependent on synthetic organic chemistry can flourish only if the importance of intensive and unremitting experimental investigation is whole-heartedly recognized and its prosecution generously encouraged.

Not only has the chemist prepared numberless compounds hitherto unknown, but he has even entered into competition with Nature herself, and has successfully broken the monopoly which heretofore she had enjoyed in the production of many compounds both of ornament and of utility. In fact, so successful has the chemist been, that not only can the artificial products, in a number of cases, compete with the natural products, but they have even driven these entirely out of the market. In this way great industries have arisen, the social and economic effects of which have been both profound and widespread.

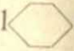
In achieving the successful building up of molecular structures, whether of naturally occurring substances or of substances hitherto unknown, the chemist may start with molecular structures which occur in Nature (*e.g.* cellulose) or which can be readily obtained from naturally occurring materials (*e.g.* benzene); or he may start from the elements or simple compounds (*e.g.* carbon from coal, oxygen and nitrogen from the air, hydrogen from water, etc.), and from these build up molecular structures of increasing diversity and complexity. In the nineteenth century, important and closely interdependent industries were established, which found their raw materials mainly in coal-tar; but in more recent years synthetic organic chemistry has drawn its raw materials to an increasing extent from petroleum.

By the distillation of coal there are produced not only the gaseous mixture so largely employed as a fuel and illuminant, but also considerable amounts of ammonia and of a thick, dark-coloured, evil-smelling liquid, coal-tar—one of the most valuable and important materials obtained by man. It is not an attractive-looking material, and yet there have been evolved from it, by the painstaking labours of a multitude of chemists, substances innumerable: many-hued dyes, which have added colour and beauty to our daily life, and pigments by which the painter can give permanence to the subtlest and most transient glories of Nature; the sweet-smelling essences of flowers; photographic chemicals; antiseptics and drugs; textile fibres, plastics and rubber-like materials, the manufacture of which has developed into enormous and rapidly expanding industries. This coal-tar is, indeed, an almost inexhaustible storehouse of raw materials for the manufacture of products of manifold variety.

By subjecting the crude coal-tar to a process of distillation, as is done in the refining of crude petroleum, various substances are obtained which distil over at different temperatures. Of these the most important are the following:

LIQUIDS	b.p.
Benzene	80·5° C. (176·9° F.)
Toluene	111° C. (231·8° F.)

SOLIDS	m.p.
Phenol (carbolic acid)	41° C. (105·8° F.)
Naphthalene	80° C. (176° F.)
Anthracene	213° C. (415° F.)

Benzene, C_6H_6, or benzole, as it is frequently called in commerce, forms the starting-point in the manufacture of aniline (which can be regarded as benzene in which one of the atoms of hydrogen is replaced by the group NH_2); and this, in turn, is the starting-point in the preparation of a large number of dyes—the aniline dyes. These aniline dyes, which were the first synthetic dyes to be prepared, constitute, however, only a part of the total number of dyestuffs which are now manufactured from coal-tar products. Benzene is an important raw material in chemical industry. When the hydrogen atoms at two opposite corners of the benzene hexagon are replaced by chlorine atoms, one obtains *paradichlorobenzene* (ClCl), which is a powerful moth repellent.

Toluene, $C_6H_5{\cdot}CH_3$ (commercially, toluole), is used as a raw material in the manufacture not only of dyes, but also of the powerful high explosive, trinitrotoluene or T.N.T. As the formula indicates, the structure of toluene is that of benzene in which one hydrogen atom is replaced by the methyl group (CH_3). To satisfy the very large war demand for toluene, this hydrocarbon had also to be produced from petroleum.

Phenol or *Carbolic Acid*, $C_6H_5{\cdot}OH$, is a well-known antiseptic, and is also the starting-point in the preparation of the explosive, picric acid, lyddite or melinite. It is also used in the manufacture of dyes and of plastics.

Cresols, $CH_3{\cdot}C_6H_4{\cdot}OH$, of which there are three isomeric forms, also occur in coal-tar and are largely used in the preparation of antiseptics (*Lysol*, *Jeyes' Fluid*, etc.) and for the production of plastics.

Naphthalene, $C_{10}H_8$, is a valuable constituent of coal-tar. Its molecular structure is represented by two benzene hexagons joined together. It is the raw material chiefly employed in the manufacture of indigotin. When naphthalene is heated with hydrogen under pressure and in presence of nickel as catalyst, hydrogenation takes place and the important solvents *tetralin*, $C_{10}H_{12}$, and *decalin*, $C_{10}H_{18}$, are obtained. By the action of chlorine on naphthalene, non-inflammable waxes (*e.g. Seekay*) are formed.

Anthracene, $C_{14}H_{10}$, is the raw material employed in the manufacture of a large number of important dyes, the most familiar of which is the red dye, alizarin, or Turkey red. Its molecular structure is represented by three benzene hexagons joined together.

Important as these different substances are, they constitute only a small part of coal-tar, the amounts in which they occur being, moreover, dependent not only on the nature of the coal used but also on the temperature at which the coal is carbonized. Thus, benzene and toluene together constitute about 3 per cent., phenol about 1 per cent., naphthalene about 5 per cent., and anthracene about 0·5 per cent. of the coal-tar formed in gas manufacture. By the distillation of one ton of coal, therefore, we should obtain the above constituents in the following quantities, roughly:

Benzene and Toluene	3½ lbs.
Phenol	1¼ lbs.
Naphthalene	6 lbs.
Anthracene	10 oz.

THE COAL-TAR DYES

Until the middle of last century, men were dependent for all the dyes with which they coloured their bodies or their garments on colouring matters which were chiefly of animal and vegetable origin: the colouring matter of logwood and of safflower; the animal dyes, kermes and cochineal; the blue dye, indigo or woad, with which our ancestors in these islands are said to have stained their bodies; the red dye, alizarin, obtained from the root of the madder plant, once extensively cultivated in Southern Europe; and the costliest of all dyes, the most famous dye of the ancient world, Tyrian purple, obtained from a shell-fish (*Murex brandaris*) found on the eastern shores of the Mediterranean.

> "Who has not heard how Tyrian shells
>   Enclosed the blue, that dye of dyes
> Whereof one drop worked miracles,
>   And coloured like Astarte's eyes
> Raw silk the merchant sells?"
> (Browning: *Popularity*.)

These dyes, and a few others, were all that were available until the year 1856. In that year the first synthetic dye, the once favourite mauve, was prepared by W. H. Perkin, by the oxidation of crude aniline ($C_6H_5NH_2$), and since that time colouring matters to the number of several thousands have been synthesized by the chemist. The natural dyes are mostly of a pronounced, even crude, colour, but the products of the chemist are of an almost infinite variety; and, far outrivalling the natural dyes in range of colour and delicacy of tone, they have ousted these dyes from the dye-works. Starting from benzene, naphthalene and anthracene, constituents of the dark-coloured liquid, coal-tar, which a hundred years ago was a useless waste material and a nuisance to the gas-manufacturer, dyes and other organic compounds are now prepared in large quantities.

It is quite impossible here to enter into a discussion of the composition and constitution of the coal-tar dyes, some of which are among the most complex of the compounds of carbon; but it may be said that the technique of dye manufacture has become so perfected, and our knowledge of the variation of colour with the constitution of the compound has become so well established, that the synthetic production of new shades is no longer a haphazard process, but one of which the conditions of success are clearly known.

Although thousands of different dyestuffs have been prepared, it is in the artificial production of Nature's own colouring matters, more especially of alizarin and indigotin, that organic chemistry has achieved some of its most striking successes. Through the labours of many chemists the composition of these natural products was determined and their constitution or molecular structure unravelled; and with the knowledge thus obtained chemists succeeded in preparing these compounds artificially—not merely substitutes for or imitations of the natural products, but the actual products themselves—and that more cheaply than Nature herself can produce them.

Until about 1870, over the whole of Southern Europe, and eastwards to Asia Minor, great tracts of land, some three or four hundred thousand acres, were devoted to the growing of the madder plant; in France alone, 50,000 acres were devoted to its cultivation. When the roots of this plant were allowed to ferment, a substance, *alizarin*, so called from the name given by the Arabs to the madder root, was formed. This substance was capable of dyeing cotton a bright red colour—the so-called Turkey red—and was one of the oldest of dyes and largely used in the dyeing of cotton goods. But these madder fields have now all disappeared; for when the composition and nature of this dyestuff had once been ascertained, it was not long before chemists discovered a method by which the dye could be manufactured from what was then practically a waste material, anthracene, one of the constituents of coal-tar. By a series of comparatively simple reactions one could pass from the hydrocarbon anthracene ($C_{14}H_{10}$) to anthraquinone ($C_{14}H_8O_2$), and from anthraquinone to dihydroxyanthraquinone or alizarin [$C_{14}H_6O_2(OH)_2$]. More recently, a new and more economical process was introduced and anthraquinone is now produced by allowing benzene and phthalic anhydride (p. 222), obtained from the more abundant hydrocarbon naphthalene, to react together in presence of aluminium chloride as catalyst. The anthraquinone is then converted into alizarin. In this way the madder dye can be manufactured much more cheaply than Nature can produce it, and the madder fields of Southern Europe exist no more.

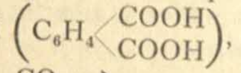
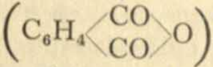
Similar social-economic effects have been produced in India, which was for long the chief home of the indigo-bearing plants. Known for over three thousand years, indigo was obtained from various species of *Indigoferæ*, cultivated more especially in India. The woad (*Isatis tinctoria*), from which indigo is obtained, was cultivated in Europe even as late as the seventeenth century, and its cultivation lingered on in the Eastern Counties of England until comparatively recent years. In the sixteenth century, with the opening up of trade with the East, the superior Indian indigo began to make its appearance in Europe, and although the use of the 'devilish drug' was at first prohibited by law, the ban was removed in the eighteenth century.

Down to near the beginning of the present century the Indian indigo plantations controlled the markets of the world. In 1896–7, India produced over eight thousand tons of indigo, the value of which was £4,000,000. It was a valuable prize, therefore, which the German dye-manufacturers set themselves to win, and after seventeen years of effort the genius and resourcefulness of their chemists won the day. In 1897, synthetic indigotin[1] was placed on the market in competition with the product from the Indian plantations, which it has almost entirely replaced; and more than a million acres of land, formerly devoted to the production of indigo, are now given over to the growing of food.[2]

Since the industrial production of indigotin involves a considerable number of different processes, and requires the use of a number of different substances, of which sulphuric acid, ammonia, chlorine and acetic acid are the chief, the success of

[1] Indigo, the dye material obtained from the indigo plant, is not a single substance but a mixture, the chief constituent of which is the blue dyestuff indigotin. It is on this difference between indigo and synthetic indigotin that the difference between the dyeing power and quality of (so-called natural) indigo and synthetic indigotin (wrongly called synthetic indigo) depends.

[2] In 1954–55, 11,500 acres were still under indigo cultivation in India.

the synthesis as a whole depends on the success with which each step of the process can be carried out, and on the cost of the substances employed. The starting-point in the manufacture is the hydrocarbon naphthalene, familiar to all on account of its use as a moth repellent; and the first step in the synthesis of indigotin is to convert this naphthalene into a compound called phthalic acid  $\left(C_6H_4{<}\begin{matrix}COOH\\COOH\end{matrix}\right)$, and then into phthalic anhydride  $\left(C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O\right)$. This, it was known, could be done by heating the naphthalene with strong sulphuric acid; but when the manufacturer attempted to make use of this fact, he found that although the desired conversion did indeed take place, it did not proceed sufficiently readily and the cost of carrying out this first step in the process was so great that it would have rendered the industrial production of indigotin unremunerative. But here a lucky accident came to the assistance of the manufacturer, for, through the accidental breaking of a thermometer, it was discovered that mercury acts as an efficient catalyst in the conversion of naphthalene to phthalic acid, facilitating the process to such a degree as to allow it to be carried out with commercial success. The method is, however, no longer used, and naphthalene in the state of vapour is now oxidized to phthalic anhydride by the oxygen of the air with the help of a catalyst, vanadium pentoxide.

A broken thermometer sealed the fate of the Indian indigo plantations! The successful industrial production of indigotin, however, depended also on improvements in the manufacture of the various chemicals employed. Thus the demand for a very powerful sulphuric acid—pyrosulphuric acid or 'oleum'—and the fact that during the process of heating it with naphthalene large quantities of sulphur dioxide are formed, led to the development of a new method of making the acid, namely, the 'contact process' to which reference was made in *Chapter* 8. For the production of chlorine, also, of which enormous quantities are required, the old method of obtaining the gas from hydrochloric acid was useless, and was replaced by the electrolysis of a solution of common salt, the chlorine being then obtained in a pure state by liquefaction. The ammonia may be obtained, as we have seen, as a product of the distillation of coal, but is mainly produced by direct synthesis from nitrogen and hydrogen; and the acetic acid is obtained by the distillation of wood, and from acetylene.

Although it is not possible to enter into a detailed discussion of the practical process of dyeing, it is of interest to note that the process is different in the case of indigo and other so-called vat dyes, from what it is in the case of other dyestuffs (*see* p. 190). On account of its insolubility, the indigo is first converted into a colourless compound, called indigo-white, which is soluble in alkalis. After the material to be dyed has been immersed in this solution, it is removed and exposed to the air, whereby the oxygen of the air oxidizes the colourless indigo-white to indigo-blue. The dye is, therefore, developed in the fibre after its removal from the bath. The vat dyes, it is interesting to note, have now been obtained in a soluble form and so have become available for dyeing wool and silk which are destroyed by the strongly alkaline solutions formerly required. Important as has been the role played by indigo in the past, this dye, like other dyes, is always under peril of being replaced by newer and better synthetic dyes.

Closely related, chemically, to indigo, is that other ancient dye, Tyrian purple, which is secreted by certain species of marine snail, the *Murex brandaris* and *Murex trunculus*, found, more especially, on the shores of the Mediterranean. On investigation, it was ascertained that this 'dye of dyes, whereof one drop worked miracles,' is a compound of indigotin with bromine, a compound which can be prepared synthetically with comparative ease. The costliness of this natural dye was almost proverbial, and the reason for this is not far to seek; for the colouring matter obtained from the glands of twelve thousand shell-fish by the German chemist who investigated the dye, amounted only to about twenty-three grains, and the estimated cost of the dye was nearly £60 an ounce.

During the present century many synthetic dyes of varied constitution, with very valuable properties and covering a wide range of shade and colour, have been produced. Thus, the so-called indanthrene dyes are distinguished by their great fastness to light and are used for dyeing various 'fadeless' fabrics; and other important series of dyes have been produced for the dyeing of synthetic fibres, such as rayon, nylon and terylene.

SYNTHETIC PERFUMES

For thousands of years the volatile substances to which the different flowers and plants owe their odours have been obtained by distillation or by extraction by means of solvents. During the years that have passed, however, the secrets of Nature have been largely unveiled, and the chemical laboratory has become odorous as a garden and filled with the perfumes of violet and rose, heliotrope, lilac, hyacinth and orange blossom; and from the stills of the chemist there flow liquids the flavours of which imitate those of the apple, pear, pineapple and other fruits, and which, in consequence, find application as artificial fruit essences. Although in a number of cases the synthetic perfumes and flavouring essences merely imitate the products of Nature, in other cases the chemist has succeeded in preparing the identical substances to which the flavour of the natural fruit or the perfume of the growing flower is due.

Just as W. H. Perkin was the first chemist to synthesize a dye, so he was the first chemist to prepare, in 1868, a naturally occurring perfume. This was *coumarin*, the odoriferous principle of the sweet woodruff (*Asperula odorata*) used in the preparation of the perfumes known as Jockey Club and New-mown Hay. This first synthetic preparation of a natural odoriferous principle was speedily followed by the preparation of the flavouring material, vanillin, the active principle occurring in the vanilla bean. This substance, formed by the oxidation of eugenol, the chief constituent of clove oil, is now manufactured from toluene, as raw material, and is of great commercial importance. To these earliest synthetic products numerous others have since been added, so that the main odoriferous principles of oil of wintergreen (*methyl salicylate*), oil of bitter almonds (*benzaldehyde*), hawthorn blossom (*anisic aldehyde*), lily of the valley (*terpineol*), ambergris (*ambrein*), and others, can now be prepared artificially. Other synthetic compounds, while not identical with the natural perfumes, closely resemble them in odour, and are employed in large quantities either as substitutes for the natural perfumes or for blending with them. Of these the most important are ionone, or imitation violet, imitation musk, and imitation oil of bitter almonds, or 'oil of mirbane' (*nitro-benzene*).

The synthetic production of sweet-smelling substances, often at only a fraction of the cost of the natural product, has led to a great extension in the use of such substances, more especially for the perfuming of soaps, creams and other toilet materials.

It has been pointed out that the synthetic production of the colouring matters alizarin and indigotin produced vast social and economic changes through the more or less complete supersession of natural by synthetic dyes. In the commercial production of camphor one finds another illustration of the successful synthesis of an important natural product, without, however, the same disastrous consequences to the latter.

Camphor (Japan camphor), one of the most familiar of substances, has been produced for many centuries in Japan, Formosa, and other regions of the Far East. It is found chiefly in the leaves of a species of the laurel-tree, the *Laurus camphora*, from which it is obtained by distilling the leaves or other parts of the tree in a current of steam. The camphor, being volatile, passes over with the steam and can be condensed in cooled vessels.

Camphor has for long been a highly valued substance on account of its therapeutic, disinfecting and other properties, and the demand for the compound has been very greatly increased in the past fifty or sixty years owing, more especially, to its employment in the manufacture of celluloid for cinema and photographic films and plastics. Japan had, therefore, a valuable source of revenue in her practical monopoly of the production of camphor through her possession of the plantations of the camphor-tree in Formosa, the extent of which, in the years following the Russo-Japanese War (1904–5), she very greatly increased; and the monopoly she possessed she sought to exploit to the utmost.

The substance, however, had long attracted the attention of chemists, and, in spite of the difficulty of the problem, its molecular constitution was at length unravelled and the compound prepared synthetically in 1903. Two years later, synthetic camphor, identical in all respects with the substance produced in the camphor-tree (except that the former is a racemic form and optically inactive, while the latter is dextro-rotatory), was placed on the market in competition with the natural product.

The camphor plantations have hitherto escaped the fate which befell the plantations of madder, and, so far as can be foreseen, they are not likely to suffer disaster. The reason for this, however, lies outside the control of the chemist, and is to be found in the scarcity and cost of the raw material used in the manufacture. The source of the raw material is oil of turpentine, an essential oil which is produced in trees belonging to different species of pine, and which is not only restricted in quantity, but is also subject to increase in price. The synthetic camphor, therefore, has not been able to displace the natural, but it has prevented an excessive rise in the price of the compound.

The remarkable achievements of the past century in the synthesis of dyes and perfumes, give an almost prophetic sound to the words of Lucretius: 'I tell you, barbaric robes and radiant Melibœan purple dipped in Thessalian dye of shells (and the hues which are displayed) by the golden brood of peacocks steeped in laughing beauty would be thrown aside surpassed by some new colour of things; the smell of myrhh would be despised and the flavours of honey . . . would in like sort be suppressed . . . for something ever would arise more surpassing than the rest.'

ANÆSTHETICS, DRUGS AND INSECTICIDES

The sixteenth and seventeenth centuries are regarded as marking a distinct era in chemistry, inaugurated by Paracelsus. During that period, chemistry was looked upon as the handmaid of medicine, and the study of the action of substances on the human organism and the preparation of drugs were held to be the true functions of the chemist. That was the period of what was called iatrochemistry or medical chemistry.

While the modern chemist would resent the restriction of his functions within such narrow limits, the services which chemistry has, in modern times, rendered to medicine are greater beyond comparison than all the iatrochemists were ever able to perform, or even to imagine. Not only have 'Nature's remedies,' the juices and extracts of plants, the valuable alkaloids like quinine and morphia, been exhaustively studied and the methods of their extraction improved, but they have been supplemented, in some cases even displaced, by a large array of new drugs and medicinal preparations which owe their origin to the genius and painstaking labours of chemists. The herbalist, in fact, has given place to the scientific chemist, and the manufacture of anæsthetics, hypnotics, antipyretics, and drugs for the treatment of special diseases, has developed into an industry of great importance.

Anæsthetics.—As early as 1800, Sir HUMPHRY DAVY had suggested the use of *nitrous oxide* (N_2O) or 'laughing gas,'[1] discovered by Priestley in 1772, as an anæsthetic, for which purpose, however, it was used in dentistry only some forty years later. In the period 1842–6, *ether* ($C_2H_5{\cdot}O{\cdot}C_2H_5$) came into use in America for the production of general anæsthesia; and in 1847 *chloroform* ($CHCl_3$) was introduced by Sir JAMES SIMPSON in Edinburgh. For many years these two substances were extensively used and they not only facilitated the work of the surgeon but also freed mankind from untold misery and suffering. In more recent times, not a few other compounds (ethylene, trichloroethylene or *trilene*, *pentothal*, etc.) possessing valuable anæsthetic properties have been prepared by chemists. These substances have their own characteristic effects on the human organism, and must be used with knowledge to suit the condition of the patient and the requirements of the surgeon.

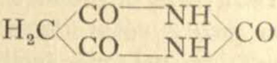
The introduction as a local anæsthetic of the alkaloid cocaine, which occurs in the leaves of the coca plant, aroused, in 1884, much interest among surgeons, and led chemists to undertake a systematic investigation of substances related structurally to cocaine, the molecular constitution of which had been elucidated in 1898. As a result, it was found that a particular physiological action is due, in many cases, to the presence of certain groupings of atoms in the molecule of a compound, and can be modified or even entirely altered by the introduction of different atoms or groups into the parent molecule, or by eliminating certain groups from it. Guided by this discovery, chemists succeeded in synthesizing a number of compounds, all of which possess local anæsthetic action. Of these, one may mention *novocaine* and *amethocaine* (known also by other names), the latter compound being, it is stated, a perfect substitute for cocaine for all purposes. It is not habit-forming.

If to the local anæsthetic a small amount of adrenaline (p. 278) is added, the blood is driven away from the injected tissues and 'bloodless' surgery becomes a possibility.

Hypnotics.—Following closely on the discovery of chloroform came the discovery of *chloral* ($CCl_3{\cdot}CHO$) and its soluble crystalline hydrate, the first hypnotic to be produced industrially. The dangers attending the use of chloral, however, led to the search for and discovery of other hypnotics which are free from its bad qualities; and at the present day quite a number of synthetic hypnotics are available. Two of the best known are barbitone or *veronal* and phenobarbitone or *luminal* (*gardenal*, *somonal*). These substances, known as barbiturates, are derived from the compound, barbituric acid,

---

[1] Prepared by heating ammonium nitrate: $NH_4NO_3 = N_2O + 2H_2O$.



$$H_2C\left\langle\begin{array}{l}CO-NH\\CO-NH\end{array}\right\rangle CO$$

By replacing the two atoms of hydrogen in the CH_2-group by two C_2H_5-groups one obtains veronal; and by replacing them by one C_2H_5- group and one C_6H_5-group one obtains luminal.

Drugs and Therapeutic Agents.—During the last quarter of the nineteenth century, chemists, seeking to obtain drugs which might supplement or replace the specific anti-malarial alkaloid quinine, prepared a number of compounds which were found to possess valuable antipyretic and analgesic (or pain alleviating) properties. Of these, one only need be mentioned here. By a modification of the molecular structure of the well-known substance, salicylic acid $\left(C_6H_4\left\langle\begin{array}{l}OH\\COOH\end{array}\right.\right)$, there was prepared acetylsalicylic acid $\left(C_6H_4\left\langle\begin{array}{l}O{\cdot}COCH_3\\COOH\end{array}\right.\right)$, or *aspirin*. As an anti-neuralgic drug, aspirin is by far the most popular and widely used of all the synthetic drugs.

Valuable, however, as these compounds were found to be as therapeutic agents, their use merely alleviated the symptoms of disease; and it was not until early in the present century that the foundations of a true *chemotherapy* were laid, by which the causes of disease were attacked by means of chemical compounds of specially planned molecular structure.

Guided by the observation that various living tissues and organisms show selective absorption for different dyes, the German physiologist and chemist, Paul Ehrlich, conceived the idea of combating diseases due to protozoal parasites by the use of substances which would be toxic for the parasites but which would not be absorbed by and would therefore not be harmful to the cells of the host. After many trials and many failures, Ehrlich was successful in finding, in 1912, in the complex, arsenic-containing compound which he called *salvarsan*, a cure for syphilis. This compound, now called *arsphenamine*, was also found to be effective in the treatment of other diseases, more especially the disfiguring and crippling disease, yaws, which were caused by parasites belonging to the class known as spirochaetes.

This first great triumph of chemotherapy was followed, in 1919, by the preparation in the United States of another arsenical drug, *tryparsamide*, which could be successfully used in the later stages of sleeping sickness (trypanosomiasis) in man. A drug of complex molecular structure, called *suramin*, prepared by German chemists, can be used as a prophylactic and as a curative agent in the early stages of the disease.

By means of these drugs, and others which chemists have prepared, trypanosomiasis in man has become amenable to control; and it is of little less importance that this disease, carried by the tsetse fly, as it affects cattle, horses and camels (in which case it is called nagana), can now also be controlled by injection of a compound, *antrycide*, produced in 1948 in the laboratories of Imperial Chemical Industries.

Since 1925, compounds containing antimony have been prepared and have been widely and successfully used as curative agents for kala-azar, a disease which is carried by the sandfly and which was for long prevalent in certain parts of India, China and elsewhere.

A still more notable and spectacular contribution to the conquest of disease has been made by the chemist in his production of synthetic compounds to take the place of quinine in the prevention and cure of malaria. This disease is stated to affect four or five hundred million people and to cause annually the death of about four million.

For many years the only control over the ravages of malaria was afforded by quinine, an alkaloid obtained from cinchona bark; and when, during World War II, the main source of supply of this substance was cut off by the Japanese invasion of Java, the position of the Allied Armies fighting in the malaria-infested regions of the Far East became precarious. Fortunately, during the inter-war years, German chemists had prepared two synthetic drugs, *plasmoquine* (or *pamaquine*), a derivative of quinoline, and the more effective *atebrine* (or *mepacrine*), a derivative of acridine. These proved to be valuable substitutes for quinine. Tablets of atebrine, packed between thin sheets of the plastic polythene, to protect them from moisture, were issued to the British and Allied troops in Burma and the Far East. They were an important factor in securing victory over the Japanese.

Valuable as mepacrine proved itself to be, a new drug, *paludrine*, prepared in 1945 by the chemists of Imperial Chemical Industries, has been found to be more effective than quinine and mepacrine as a prophylactic and more powerful in destroying the parasites and in controlling the symptoms of malaria.

Since 1935, great advances have been made, and one of the most remarkable discoveries in the domain of chemotherapy has been that of the therapeutic value of a number of compounds belonging to what is called the sulphanilamide ($NH_2{\cdot}C_6H_4{\cdot}SO_2 NH_2$) group, and generally spoken of as *sulpha-drugs*. Sulphanilamide itself arrests the action[1] of the streptococci which are the cause of puerperal fever, scarlet fever and erysipelas, and is also of value in preventing sepsis in wounds. It was found, however, as the result of chemical investigation by the research staff of Messrs. May and Baker, that if one of the hydrogen atoms of the $—SO_2NH_2$ group is replaced by various molecular structures (pyridine, thiazole, guanidine, etc.), the effectiveness and range of usefulness of the sulpha-drugs could be extended. Thus, *sulphapyridine* (M. and B. 693) and *sulphathiazole* (M. and B. 760) are effective in combating not only streptococci but also pneumococci and meningococci, the organisms responsible for pneumonia and meningitis. Sulphaguanidine is especially valuable in the treatment of dysentery.

Through the introduction of the sulpha-drugs, regarded, popularly and not without reason, almost as miracle-working drugs, the treatment of bacterial diseases in man has, since 1935, been completely revolutionized; and a very notable reduction in the number of deaths due to puerperal fever, pneumonia, pneumococcal meningitis and other diseases has been effected.

To one other group of sufferers, the sufferers from the disease of leprosy, the chemist brings a message of confidence and hope. Until recent years this very old and, as it was called, 'loathsome disease' was considered to be incurable, although a certain alleviation of suffering was afforded by treatment with Chaulmoogra oil; and the leper, cut off from his fellow-men or segregated in colonies, was regarded almost

---

[1] The sulpha-drugs are bacteriostatic, not bactericidal, in action; that is, they prevent the multiplication and arrest the action of the bacteria, which are then destroyed by the leucocytes of the blood.

> 'As dead from all the human race as if beneath the mould.'

Now, however, by means of the compound called *dapsone* (*avlosulfon*), $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot C_6H_4 \cdot NH_2$, or one of its derivatives, *e.g. solapsone* (*sulphetrone*), compounds belonging to the class known as sulphones, a cure, slow perhaps but sure, can usually be effected.

During the present century the use of synthetic drugs has undergone an extraordinary development. More than half of the four hundred and forty substances described in the 1948 edition of the British Pharmacopoeia were products of the laboratory and factory. The wonderful contributions which chemists have thus made to the alleviation of pain, the maintenance of health and the conquest of disease form one of the most notable features of the history of medicine. By none has a greater service been rendered to mankind than by chemists.

In man's fight against disease his most spectacular success, perhaps, is to be found in the discovery of substances which are produced by living organisms and which inhibit the growth of or even destroy bacteria and other disease-provoking micro-organisms. These are the substances called *antibiotics*. In their production the chemist is but the partner of the biologist.

One day in 1929, through the open window of the laboratory of Sir ALEXANDER FLEMING, bacteriologist at St. Mary's Hospital, London, a stray spore of a mould blew in and fell by chance on a dish containing bacteria growing in a culture medium. Here also the mould grew, and where it grew Fleming noticed that the colonies of bacteria (staphylococci) disappeared. In this way it was discovered that the mould, identified as *Penicillium notatum*, produces during its growth a substance which has powerful bacteriostatic, and even bactericidal, properties. To this substance Fleming gave the name *penicillin*. Thus again did a 'happy accident' help the alert and trained investigator to his discoveries.

TITUTE OF EDUCATION FOR
Dept. of Extension
SERVICE

For a number of years the discovery lay dormant, but in 1940 the method of isolating the sensitive penicillin was developed by a team of workers under Sir HOWARD FLOREY, at Oxford, and large-scale production, in thousands of small culture vessels, was carried out in Britain and the United States. By D-day in 1944 an adequate supply for all the Allied Armed Forces was available. Production is now carried out in various countries by growing an improved strain of the mould in large tanks of culture medium under rigorously controlled conditions.

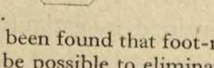
Although a laboratory synthesis of penicillin has been devised there is little probability that it will ever replace the processes of bio-synthesis by the growing mould.

Through the discovery and production of penicillin there was put into the hands of the surgeon and physician a unique antiseptic which, while non-toxic to the patient, is extremely efficacious in rendering harmless the micro-organisms responsible for pus formation, gas gangrene and other wound infections which, in the past, have been the cause of many deaths. Penicillin, also, may be used beneficially in the treatment of diphtheria, tetanus, boils, carbuncles and impetigo; and it is effective against the spirochaetes of syphilis and yaws.

Since the discovery of penicillin, biochemists have succeeded in isolating many other antibiotics, some of which have valuable therapeutic properties. Of these one may mention: *streptomycin*, which has proved to be efficacious in the treatment of human tuberculosis;[1] *chloramphenicol* (chloromycetin), a substance not only produced by a mould but now also manufactured synthetically; *aureomycin* and *terramycin*. The last three antibiotics have proved to be valuable therapeutic agents in the treatment of a wide range of diseases, due both to streptococcal and staphylococcal infections. More especially have they proved of value in the treatment of typhus and Rocky Mountain spotted fever, diseases caused by rickettsiae, organisms intermediate between bacteria and the viruses.[2]

It is not without interest to note that the antibiotics are

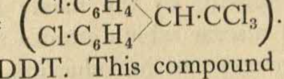
---

[1] Some success in the treatment of tuberculosis has also been obtained with *isoniazid*,  $\mathrm{N}\langle\quad\rangle\mathrm{CO{\cdot}NH{\cdot}NH_2}$, a compound of isonicotinic acid and hydrazine.

[2] It has been found that foot-rot of sheep responds to chloramphenicol, and it may now be possible to eliminate the disease from flocks.

valuable not only as therapeutic agents, but also as growth stimulants in farm stock, *e.g.* pigs and poultry. Addition of aureomycin, for example, to the animal feed is stated to have increased the rate of growth of hogs by as much as 50 per cent.

Insecticides.—Since it has been found that many protozoal and bacterial diseases are transmitted from man to man by insects, one may combat these diseases not only by means of prophylactic drugs but also by the destruction of the insect carriers. For many years one has used, for the destruction of mosquitoes and other insects, an extract of pyrethrum flowers (containing two active ingredients, the *pyrethrins*), dissolved in kerosine (as in the familiar 'flit'), or in the liquid *freon* (p. 178), as well as an extract of derris root, the chief active principle of which is *rotenone.* The larvæ of mosquitoes, on the other hand, have been destroyed by spraying the breeding areas with kerosine or with Paris green, an organic compound containing arsenic and copper.

During the war of 1939–45, however, supplies of the above insecticides were largely cut off, owing to the entrance of Japan into the war, and it became necessary to obtain other insecticides to cope not only with mosquitoes but also with other insect carriers of disease. Of these, especially in times of war, the louse, carrier of typhus, which in the past has decimated armies and civilian communities, is one of the most important. During the war, therefore, chemists and technologists in Britain and America developed the industrial manufacture of an insecticide first prepared in Switzerland some years previously and known to chemists by the somewhat formidable name of diparadichlorodiphenyltrichloroethane  $\left(\begin{matrix}Cl\cdot C_6H_4\\ Cl\cdot C_6H_4\end{matrix}\!>CH\cdot CCl_3\right)$. It is now referred to generally as DDT. This compound has been found to be an insecticide of remarkable potency and persistence, although it does not possess the rapid 'knock-down' property of the pyrethrins. It can be used for the destruction of the insect carriers of malaria, yellow fever, sleeping sickness (tsetse fly), dysentery (house fly), typhus (louse), plague (flea), etc. In 1943 it had one of its greatest triumphs in successfully combating, by the killing off of body lice, an epidemic of typhus which broke out in Naples. Over a million of the civilian population were disinfested by DDT. The freedom of the men of the Allied forces from lice infestation was due largely to the impregnation of their clothing with DDT.

In 1942, an even more powerful insecticide than DDT was introduced. This substance, to which the name *gammexane* was given, is one of the four isomeric forms of the compound, benzene hexachloride ($C_6H_6Cl_6$), conventionally called BHC. Like DDT, gammexane is a solid and can be used either as a dusting powder, mixed, say, with gypsum, or as a spray, when dissolved in a suitable solvent. Like DDT, gammexane has a persistent rather than an immediate knock-down action, and is outstanding in its toxicity to locusts.[1]

Mention may be made of two other insecticides, *aldrin* and the more powerful *dieldrin*, the latter prepared from the former by means of hydrogen peroxide. These are highly chlorinated compounds and are effective against many insects, including the locust. In 1953 dieldrin dealt very effectually with the plague of seaweed flies at Brighton. It has also been found very potent not only against the mosquitoes which are the carriers of malaria but also against those which are the carriers of the disease filariasis.

Not a few other insecticides have been produced for the protection, more especially, of food crops, fruit trees and forests. Some of these are selective in action and spare harmless or beneficial insects, such as bees and ladybirds.

Compounds, generally containing phosphorus, have also been prepared which can be taken up from the soil by plants and thus enter the cell sap. Insects sucking the sap of these plants are poisoned. Such insecticides have been used with success for controlling the spread, by the mealy bug, of 'swollen shoot disease,' a virus disease which attacks the cocoa-tree.

With the discovery and introduction of the newer and more potent insecticides, highly successful campaigns have been instituted for the elimination of the insect carriers of malaria, sleeping sickness, etc. In several countries, by the use of drugs and insecticides, the incidence of malaria has been markedly diminished, and even reduced to zero. Similarly, one may hope that by the use of insecticides and of the prophylactic, antrycide, the tsetse fly may be destroyed and trypanosomiasis (nagana) in cattle may be abolished. Thus there would be made available for stock-raising millions of square miles of grass land in Africa, at present under the frustrating occupation and domination of the tsetse fly (Plate 32).

---

[1] During the Korean war it was reported that gammexane, but not DDT, was effective against Korean lice.

In concluding this chapter, it may be mentioned that two compounds, *dimethyl phthalate* and *dibutyl phthalate*, although not insecticides, have been found of value for repelling attacks of midges, gnats, mosquitoes, scrub mites, etc. The compounds are prepared from methyl and butyl alcohols and phthalic acid.

Chapter 14

ARTIFICIAL FIBRES AND PLASTICS

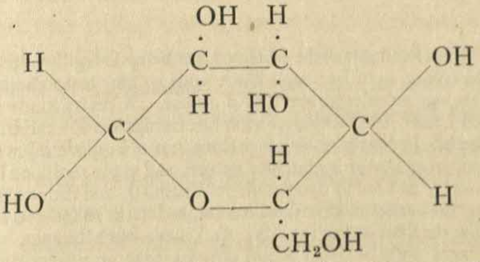
MANY naturally occurring materials, *e.g.* cotton, silk, wool, exist in the form of fibres; and from early times man has made use of these fibres for weaving into textiles. Although these fibres differ in chemical nature and composition, X-ray examination has shown that they are all made up of long molecular chains, giant molecules, or *macromolecules*, built up of hundreds or thousands of smaller units, joined together like the links of a chain. One has, then, to think of these natural fibres as consisting of bundles of long-chain molecules, arranged parallelwise, with forces of attraction holding the chains together. It is on the existence of long-chain molecules, packed closely side by side, that the strength of a fibre depends.

The commonest natural fibre, and the most abundant naturally occurring organic compound, is *cellulose*. It is one of the most important and valuable substances in present-day civilization, and is employed in the manufacture not only of cotton and linen textile materials, but also of explosives, paper, and other materials to some of which we shall refer later.

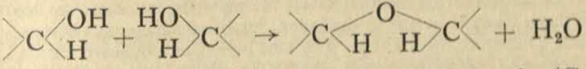
The purest naturally occurring form of cellulose is cotton, the hairy material which covers the seeds of various species of the cotton plant (*Gossypium*). When this has been chemically treated with alkalis and bleaching agents, and with acids, in order to remove various organic and mineral impurities, the product constitutes what is called cellulose.

Chemically, cellulose belongs to a group of compounds consisting of carbon, hydrogen and oxygen, in which the hydrogen and oxygen are present in the proportion of two atoms of the former to one of the latter. Since this is the proportion in which these two elements combine to form water, it was thought, erroneously, that cellulose and the other compounds belonging to that group were compounds of carbon with water, and so the name *carbohydrate* was applied to them. The different sugars, such as glucose and sucrose (cane and beetroot sugar), and also starch and a number of other substances, belong to the class of the carbohydrates; and in cellulose the carbon, hydrogen and oxygen are united in the proportions of six atoms of carbon, ten atoms of hydrogen, and five atoms of oxygen ($C_6H_{10}O_5$).

The molecule of cellulose is very large and may be regarded as built up of molecules of glucose, $C_6H_{12}O_6$, represented by the graphic formula:



These molecules are formed into a chain by a process of *condensation*; that is, by the elimination of a molecule of water between each pair of glucose molecules. Thus:



$$>\mathrm{C}<^{\mathrm{OH}}_{\mathrm{H}} + {}^{\mathrm{HO}}_{\mathrm{H}}>\mathrm{C}< \;\rightarrow\; >\mathrm{C}<_{\mathrm{H}}{}^{\mathrm{O}}{}_{\mathrm{H}}>\mathrm{C}< + \mathrm{H_2O}$$

Cellulose is therefore represented by the formula $(C_6H_{10}O_5)_n$, where n is about 10,000.

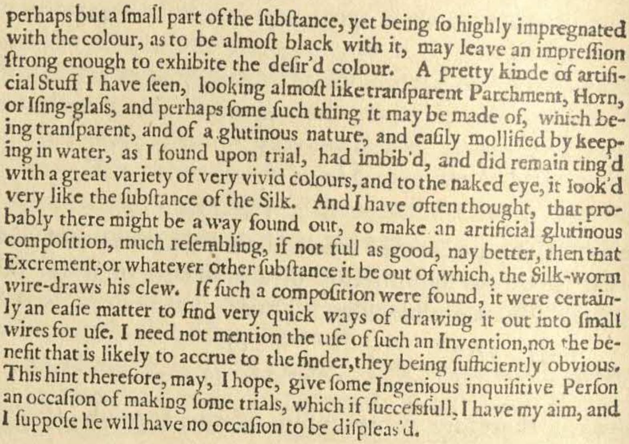
For most industrial purposes, apart from the manufacture of textiles and explosives, cellulose from wood is employed. For the production of this, wood is boiled under a pressure of several atmospheres with a solution of calcium bisulphite.[1] The wood fibre is thereby broken up chemically, with production of cellulose ('sulphite pulp').

The process of condensation of glucose molecules to form cellulose can be reversed by heating cellulose, under pressure, with dilute sulphuric acid. The cellulose undergoes *hydrolysis*; that is, water is taken up and the molecule of cellulose is decomposed into its constituent glucose molecules. Hydrolysis of cellulose also takes place in the process of producing sulphite pulp, and the glucose formed in this process is used for the production of alcohol by fermentation (*Chap.* 15). By the acid hydrolysis of wood there are also formed acetic acid and a sugar known as *xylose*, $C_5H_{10}O_5$, which is suitable for consumption by diabetics. Great possibilities are thereby opened up for the development of forest products.

---

[1] This is produced by passing sulphur dioxide into milk of lime (a suspension of slaked lime, or calcium hydroxide, in water).

As long ago as the seventeenth century, threads 'resembling silk' were being sold in England, and Dr. ROBERT HOOKE, in 1664, put forward in his *Micrographia* the suggestion that it might be possible to make an 'artificial glutinous composition' resembling silk. This suggestion was realized in 1883, by Sir JOSEPH WILSON SWAN, who was the first to produce filaments by squirting solutions of nitro-cellulose and the first to de-nitrate the filaments produced. The incentive which led Swan to his invention was the demand for a continuous filament for use in the recently introduced electric light bulbs; but Swan also soon realized the possible uses of these filaments for textile purposes, and gave them the name of 'artificial silk.'



perhaps but a ſmall part of the ſubſtance, yet being ſo highly impregnated with the colour, as to be almoſt black with it, may leave an impreſſion ſtrong enough to exhibite the deſir'd colour. A pretty kinde of artificial Stuff I have ſeen, looking almoſt like tranſparent Parchment, Horn, or Iſing-glaſs, and perhaps ſome ſuch thing it may be made of, which being tranſparent, and of a glutinous nature, and eaſily mollified by keeping in water, as I found upon trial, had imbib'd, and did remain ting'd with a great variety of very vivid colours, and to the naked eye, it look'd very like the ſubſtance of the Silk. And I have often thought, that probably there might be a way found out, to make an artificial glutinous compoſition, much reſembling, if not full as good, nay better, then that Excrement, or whatever other ſubſtance it be out of which, the Silk-worm wire-draws his clew. If ſuch a compoſition were found, it were certainly an eaſie matter to find very quick ways of drawing it out into ſmall wires for uſe. I need not mention the uſe of ſuch an Invention, nor the benefit that is likely to accrue to the finder, they being ſufficiently obvious. This hint therefore, may, I hope, give ſome Ingenious inquiſitive Perſon an occaſion of making ſome trials, which if ſucceſsfull, I have my aim, and I ſuppoſe he will have no occaſion to be diſpleas'd.

PASSAGE FROM HOOKE'S *Micrographia*

Swan's process was adapted commercially in France by Count HILAIRE DE CHARDONNET, who, in 1889, exhibited in Paris a material which, in its general appearance, imitated in a remarkable manner the fibre spun from the glands of the silkworm.[1]

---

[1] True silk belongs to a class of substances known as proteins, and contains nitrogen as well as carbon, hydrogen and oxygen.

Nitro-cellulose (cellulose nitrate), as we have seen, can, when suitably prepared, be dissolved in a mixture of alcohol and ether, and when the somewhat viscous liquid which is thus obtained is squirted through fine openings, and the jet of liquid allowed to pass through water, thin threads or filaments are formed. By treating these threads with certain solutions, *e.g.* a solution of sulphide of ammonium, the nitrate groups (NO_3), to the presence of which the nitro-cellulose owes its ready inflammability, are removed, and one obtains a regenerated cellulose, the natural structure of which has, however, been destroyed by the treatment to which it has been subjected. Threads or filaments so produced have all the superficial appearance and lustre of silk, and it was by this process that the fibre produced by the silkworm was first imitated and counterfeited in a commercially successful manner.

The method by which most of the imitation silk, or *rayon*,[1] as it is now called, is made at the present day, the so-called viscose process, was invented by the English chemists, C. F. Cross and E. J. Bevan. As raw material for this process, wood pulp, prepared by the maceration and chemical treatment of wood, is used. This pulp is treated with a solution of caustic soda and then with the liquid called carbon disulphide, whereby a thick syrup-like mass (*viscose*) is obtained. By forcing this material through minute jets, or spinnerets, into a bath containing sulphuric acid, sodium sulphate, zinc sulphate and glucose, the viscose filament is coagulated and reconverted into cellulose. Silky filaments are thus produced which can be spun into threads or yarn suitable for weaving. Although, originally, the popularity of rayon depended mainly on its lustrous appearance, in which it is superior to natural silk, de-lustred rayon, or rayon with a dull lustre, was introduced in 1926 and rapidly gained popularity. To produce a rayon with dull lustre, the viscose is forced through spinnerets into a solution containing a white pigment (*e.g.* titanium oxide).

Although costing very much less than silk, rayon has not been found to enter into direct competition with the natural product; but for use in the production of articles of apparel, whether woven or knitted, of embroideries and laces, imitation furs and tapestries, it has developed for itself, and by reason of its own distinctive properties, a rapidly expanding field of usefulness.

---

[1] Rayon is a term applied to artificial fibres of cellulosic origin.

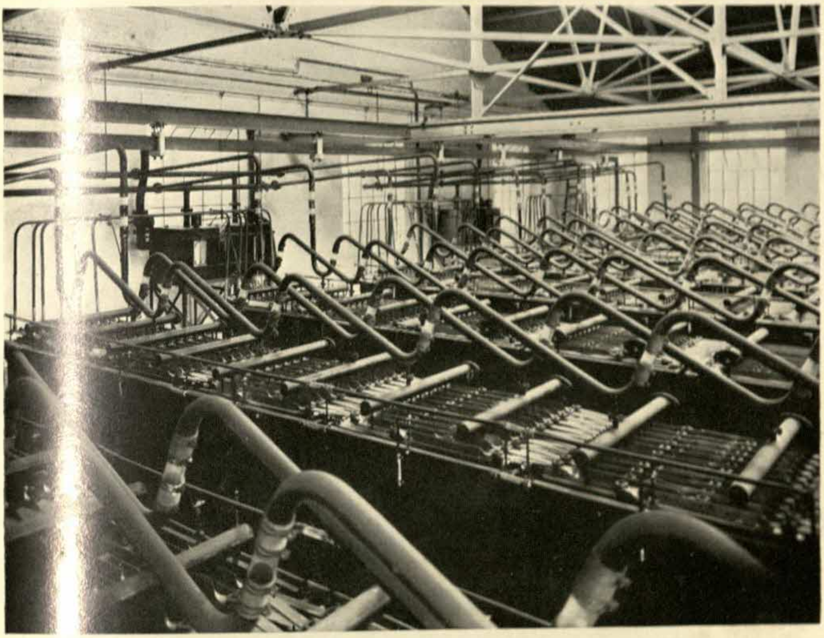
Another type of artificial fibre has also come into use under the name of *Celanese* or *acetate rayon*. Unlike the viscose rayon, Celanese does not consist merely of transformed cellulose, but is a compound of cellulose with acetic acid, cellulose acetate. A viscous solution of cellulose acetate in acetone is forced through spinnerets and the acetone is removed from the issuing filaments by means of warm air.

When Celanese is treated with a dilute solution of alkali, it undergoes hydrolysis; the acetate groups are removed and the Celanese is reconverted into cellulose. If, at the same time, the fibre is stretched, so as to bring about a favourable arrangement of the long-chain molecules, its strength is so greatly increased that, weight for weight, it is stronger than the strongest steel. Ropes made of this regenerated and stretched cellulose (known as 'fortisan') were used, during the war, for towing gliders carrying airborne troops.

While, in the early days of the rayon industry, the filaments from the spinnerets were spun into yarn, now, nearly half of the total amount of rayon produced is made into *staple fibre* by cutting the filaments into short lengths, like the fibres of cotton and wool. The staple fibre is then spun, either alone or mixed with other natural or artificial fibres, on a cotton or woollen mill, and a yarn obtained with which the textile manufacturer can obtain novel and interesting effects. Staple fibre, also, produced from de-lustred rayon and specially crimped or curled, is used as a wool substitute. Fibres which may be used as wool substitutes and which possess the dyeing properties of wool in varying degrees are also produced, under the name of *Rayolanda*, by impregnating the viscose filaments with synthetic resins.

One should not fail to realize that the invention of rayon has not only given rise to an industry of great magnitude and economic importance, but has also brought about social reactions of a very marked character. By making a material, having much of the attractiveness of silk, readily available for textiles of varied character and use, for stockings and other articles of apparel, a profound change has been effected in the taste, outlook and way of life of large sections of the community.

Viscose is used for the production not only of rayon but also of a transparent cellulose film under the registered name of *Cellophane*. From a slit pouring machine a continuous band of



29. PRODUCTION OF HYDROGEN AND OXYGEN BY ELECTROLYSIS

30. FIGURE OF EROS ON SHAFTESBURY FOUNTAIN, LONDON

31. LOUIS PASTEUR

32. SPRAYING INSECTICIDES FROM A HELICOPTER

viscose is formed which is then passed through a salt and acid solution in order to decompose the viscose. The sheet of transparent cellulose is then bleached with hydrogen peroxide, washed, and dried in warm air. Thin sheets of Cellophane are now much used for wrapping foodstuffs and other materials, and also by druggists for capping the stoppers of bottles. Placed in position while wet, it shrinks greatly on drying and so fits tightly to the bottle.

Cellulose acetate, also, is used not only as a thermoplastic material (p. 244) but also, in the form of sheets reinforced with wire netting, as a substitute for glass, under the names *vimlite* and *windolite*.

The imitation silks described in the preceding pages must not be confused with the lustrous material known as *mercerised cotton*, named after JOHN MERCER, an English calico printer who, in 1844, found that, when cotton is acted on by a solution of caustic soda, the naturally flat, twisted fibres swell to a cylindrical form and become shorter. Forty-five years later, in 1889, H. A. LOWE discovered that when the cotton fibres are tightly stretched during their treatment with caustic soda solution, so that they cannot shrink, they exhibit, after washing and drying, a silky lustre, due to the reflection of light from the smooth surface of the fibre.

From very early times wool has been held in high esteem as a clothing material on account of its softness and warmth; and it was therefore natural that chemists should seek to produce an artificial fibre with wool-like properties. In 1935 such a fibre, the invention of an Italian chemist, ANTONIO FERRETTI, was placed on the market. This fibre, known as *Lanital*, is made from casein and, in its molecular structure—that of a protein—approaches more closely to wool than rayon does to silk.

Casein, which belongs to the class of compounds known as proteins, is obtained as a curd, by adding hydrochloric acid to skimmed milk. It is dispersed in a dilute solution of caustic soda and the liquid is squirted through fine perforations in a steel disc. The filaments so formed are coagulated in sulphuric acid. After drying the filaments are treated with formaldehyde and a suitable plasticiser, whereby they are hardened, rendered more elastic and more resistant to water. By treatment with chlorine, the wool-like appearance of the Lanital is accentuated. In strength, Lanital is not much inferior to wool, and is generally used in admixture with wool or cotton. It is non-creasing and does not shrink.

In 1945, the production in Great Britain of a wool-like synthetic fibre, the invention of the chemists of Imperial Chemical Industries at Ardeer, was announced. It has been given the name *Ardil* and is produced from the protein of ground-nuts or pea-nuts. An alkaline solution of the protein is extruded through spinnerets into a bath of sodium sulphate and sulphuric acid, the filaments stretched in order to increase their tensile strength and hardened in a solution of sodium chloride to which a small quantity of hydrochloric acid and of formaldehyde has been added. Ardil forms a crimped fibre with a soft, wool-like handle and, for textile purposes, is mixed with wool or other fibres.

Another valuable artificial fibre of wool-like character, known as *Vicara*, is produced in the United States from the protein of maize.

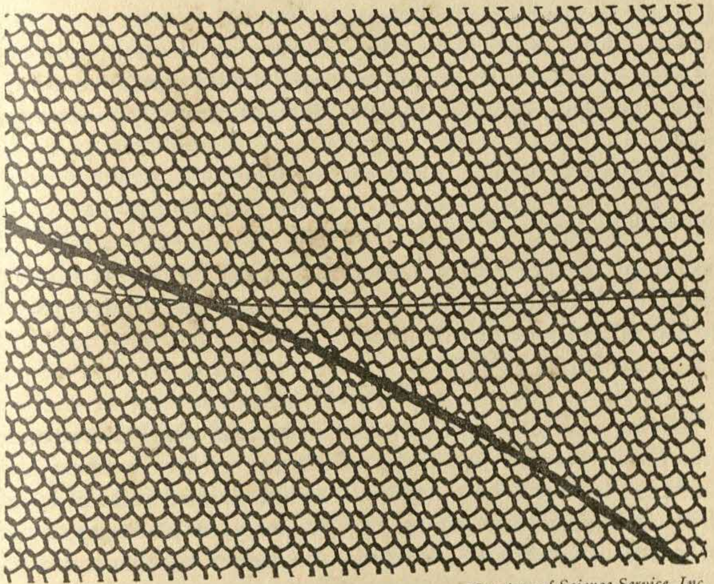
In the production of Rayon, Lanital, Ardil and Vicara, use is made of long-chain molecules—cellulose and proteins—which are found ready formed in Nature. Inevitably, however, the question arose whether the chemist could not himself produce long-chain molecules from which artificial fibres might be formed. The answer was first given by W. H. CAROTHERS, a chemist in the firm of du Pont de Nemours in America; and in 1940 there was produced the first entirely synthetic artificial fibre to which the name *nylon*[1] was given. On allowing the compound hexamethylene diamine, $NH_2{\cdot}(CH_2)_6{\cdot}NH_2$, to react with adipic acid, $COOH{\cdot}(CH_2)_4{\cdot}COOH$, condensation (p. 237) takes place with formation of

$$NH_2{\cdot}(CH_2)_6{\cdot}NH{\cdot}CO{\cdot}(CH_2)_4{\cdot}COOH$$

and by repeating the process time after time a highly complex molecule with the protein-like structure $[-NH{\cdot}(CH_2)_6{\cdot}NH{\cdot}CO{\cdot}(CH_2)_4{\cdot}CO-]_n$ is built up, the molecular weight of the compound being greater than 10,000. In the molten state it can be extruded through perforated plates to form strong and elastic filaments with a silky lustre. By drawing out these extruded filaments to about four times their original length, the long-chain molecules are orientated and the tensile strength is greatly increased. Transparency and a high degree of lustre are also developed. On account of its great tensile strength, fabric woven of nylon yarn has found extensive use for parachutes; and ropes of nylon were used during the war for towing gliders. A nylon rope, half an inch in diameter, will support a weight of three tons. Weight for weight, it has a greater tensile strength than steel.

---

[1] Nylon is used as a generic name. Different varieties of nylon can be produced.



[*Courtesy of Science Service, Inc.*

FINE MESH OF NYLON STOCKINGS, CONTRASTED WITH A HUMAN HAIR (FINE HORIZONTAL LINE) AND A PIECE OF NO. 60 SEWING COTTON (HEAVY DIAGONAL LINE)

The introduction of nylon, especially in the form of ladies' stockings, caused an unprecedented sensation; and alone, or mixed with other fibres, it is extensively used for a great variety of textiles. Nylon can also be obtained in the form of sheets and of bristles, for use in tooth-brushes, for example. Bristles for paint-brushes, which have to have tapering ends, are also produced.

Another synthetic fibre, *Terylene*, the production of which may be regarded as a logical extension of the synthesis of nylon, was obtained by the chemists of the Calico Printers' Association, by the condensation of an acid, known as terephthalic acid, $HOOC\cdot C_6H_4\cdot COOH$ (p. 202), with the compound ethylene glycol, $HO\cdot(CH_2)_2\cdot OH$. By the elimination of one molecule of water from each pair of molecules of acid and glycol, one obtains the condensed molecule, $[-O\cdot(CH_2)_2\cdot O\cdot CO\cdot C_6H_4\cdot CO-]_n$. This new fibre is very strong and is used for the manufacture of rope, fishing lines, etc. It is also extensively used for all sorts of textiles. In America it is known as *Dacron*.

Since the product of reaction between an alcohol (compound containing an OH group) and an acid (COOH group) is called an *ester*, Terylene belongs to the class of polymeric esters, or polyesters.

Polymerized acrylic nitrile ($CH_2{:}CH\cdot CN$), which forms a molecular chain of some two thousand $\left(-\mathrm{CH}\cdot\underset{\mathrm{CN}}{\dot{\mathrm{C}}\mathrm{H}}-\right)$-units, is produced in the U.S.A. under the name *Orlon*. It is found specially suitable for outdoor furnishings, tents, awnings, etc. It may usefully be blended with wool.

PLASTICS

Among the most important of industrial synthetic products are those numerous materials which are known by the general name of plastics. These materials, although hard and rigid under ordinary conditions, exhibit the property of plasticity, or the property of undergoing deformation under mechanical stress, during some stage of their manufacture. In some cases, they are *thermoplastic*; in others, *thermosetting*. The former become plastic when heated, and can be repeatedly moulded and remoulded by the application of heat and pressure; the latter also can be moulded by heat and pressure, but undergo a chemical change under the action of heat and pass into a hard mass which cannot be softened and remoulded by the further application of heat and pressure. To the former group belongs celluloid, one of the first plastics to be introduced; to the latter, bakelite.

To whichever group they belong, plastics are compounds with large molecules, or compounds of high molecular weight. In some cases, the large molecules have been built up by nature and exist in the raw material (*e.g.* cellulose) used in the manufacture of the plastic; but in most cases, the large molecules are formed during manufacture, either by the combining together of a large number of small molecules, that is, by *polymerization*, or by a chemical reaction in which a molecule of water is eliminated between each pair of simple molecules, that is, by *condensation*. The formation of polythene (p. 250) is an example of the former process; the formation of nylon (p. 242), an example of the latter.

Although, no doubt, plastics were at first introduced as substitutes for naturally occurring materials—bone, ivory, gums and resins—they must no longer be so regarded; and certainly not as substitutes which are inferior to natural products. Plastics are new materials made available to man, materials which have their own distinctive and valuable properties. For many purposes, they are superior to and have displaced wood, metal and stoneware, and they have found very widespread and varied use as new constructional materials. Their production has now become a vast and rapidly expanding industry.

In the middle of last century, the supply of billiard balls was threatened owing to a shortage of elephant tusks; and an American newspaper offered a prize of $10,000 for the most successful ivory substitute. Working under this incentive, two brothers HYATT, of Albany, N.Y., in 1869, made use of the fact, discovered in 1865 by ALEXANDER PARKES of Birmingham, that if camphor is added to a mixture of nitro-cellulose and alcohol, a hard, horn-like material is obtained which can readily be fashioned, while hot, into articles of various shapes and forms. To this material the name *celluloid* was given.[1] Although naturally of a clear gelatin-like appearance, celluloid can easily be dyed various colours, can be rendered opaque by the addition of different substances, and can, by special treatment, be made to imitate not only such materials as bone and ivory, but also amber, tortoise-shell, marble and agate. Light in weight and not readily breakable, celluloid is used for the manufacture of photographic films, combs, knife-handles, soap-boxes, and other articles of common use too numerous to mention. It is, however, a material the use of which is not altogether free from danger, since the basis of celluloid is the highly inflammable nitrocellulose. It has, indeed, given rise to many disastrous conflagrations. To start the combustion of the celluloid, it is not necessary to bring it into contact with a naked flame. Contact for a short time with an incandescent electric-light bulb may be sufficient to start the combustion, and fires have even been caused by the accidental focusing of the sun's rays on articles of celluloid exhibited in shop windows.

---

[1] Soon after the introduction of celluloid a similar material was produced in England under the name *xylonite*.

Although the dangerous inflammability of celluloid can be reduced by the addition of various salts, dextrine and similar substances, the discovery of a material having the many good qualities of celluloid, but free from the dangers attending its ready inflammability, is clearly one of great importance. The acetate of cellulose, when mixed with suitable plasticizers, yields a material called *cellon* or *lumarith*, which resembles, and is even superior to, celluloid in its general properties, and is not inflammable. It is more elastic than celluloid, is used as a substitute for gutta-percha, vulcanite, etc., and is also used for making the bristles of hair-brushes, for the production of the imitation horse-hair of which ladies' hats are frequently made, and for the manufacture of cinematograph films. In the form of a thick viscous solution it is employed as a flexible varnish for wood, paper and metal, and as an insulating covering for electrical conductors.

If instead of mixing the nitro-cellulose with camphor so as to produce celluloid it is mixed with a drying oil, like linseed oil, and with colouring matters, and is then spread on a fabric, a sort of 'oil-cloth' is obtained; and on passing this between suitably cut rollers, the material is grained and a very good *imitation leather* is produced. Such imitation leathers are now used very extensively for the upholstering of furniture and for other purposes. It is widely used for the upholstery of motor cars, for which purpose the world's total supply of leather would be quite inadequate.

At the present time, also, nitro-cellulose is very extensively employed for the production of *collodion* (a solution of nitro-cellulose in a mixture of ether and alcohol), for use in pharmacy and as a dip for incandescent mantles. It is also used for the preparation of lacquers and enamels for wood, leather and metal. For the production of these lacquers and enamels, which are widely used for the finishing of motor-car bodies, etc., the nitro-cellulose is dissolved in a suitable solvent, and to the solution there are added a diluent, a gum or resin (dammar, mastic, shellac, etc.), a plasticizer and a pigment. The resin is added in order to give gloss, hardness and impermeability to the film, and the plasticizer, in order to prevent the film from becoming too brittle. After application, the lacquer rapidly dries and the film obtained is characterized by its hardness, toughness and resistance to scratching and rubbing. The production of satisfactory lacquers is a work of great complexity, and success has been obtained only as the result of prolonged research, deep knowledge and rigid scientific control.

The introduction of these nitro-cellulose lacquers has created a demand for a large number of solvents of different volatility, such as ethyl acetate, acetone, butyl acetate, amyl acetate, ethyl lactate, butyl lactate, etc., and for plasticizers such as triphenyl phosphate, tricresyl phosphate, diethyl phthalate. As a result of this demand, substances which formerly were laboratory products of purely scientific interest are now produced on a large scale for industrial application.

As in the case of celluloid, so also in the case of the plastic *erinoid* or *galalith*, the raw material is a natural product of high molecular weight, the protein known as casein (p. 267). Ground casein, mixed with filler and pigment, if desired, is heated and extruded by pressure in the form of a rod, or formed into sheets by pressing between metal plates at a suitable temperature. It is then 'cured' or hardened and rendered insoluble and horn-like by being soaked in a solution of formaldehyde (formalin). By suitable working it can be made to resemble bone, ivory, horn, coral, tortoise-shell, amber, etc., and is used for a great variety of articles, *e.g.* buttons, beads, umbrella handles, combs. It is non-inflammable but cannot be obtained in a form suitable for photographic films. It is sometimes mixed with another plastic, polystyrene (p. 253).

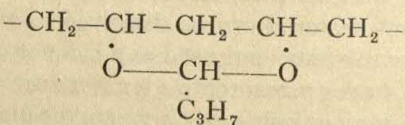
About the year 1908, the American chemist, L. H. BAEKELAND, found that on warming together phenol (carbolic acid) and formaldehyde, along with a little ammonia, which hastens the reaction, a thick gummy mass is produced. When freshly prepared this gummy material can be dissolved in alcohol, acetone and other similar solvents, and used as a lacquer or varnish; but on being heated, under pressure, to a temperature of over 100° C. or 212° F., it undergoes polymerization and changes into a hard, resin-like solid, to which the commercial name of *bakelite* is given. Bakelite is a thermosetting plastic, is infusible and insoluble in all solvents, and is the most versatile and widely used of all the synthetic resins. It is an excellent insulator for electricity, and finds, in consequence, its most important applications in the electrical industries. Bakelite may be employed for a great variety of purposes—as a substitute for amber in pipe-stems and beads; and for making buttons, knife-handles, telephone instruments and many other articles for which bone, celluloid, ebonite, or other material was formerly employed. It is not so flexible as celluloid, but it is more durable, is not inflammable, and is less expensive. In some of their most important applications, the phenol-formaldehyde resins are used along with various fibrous 'fillers'—wood-meal, cotton fibre, asbestos, etc.—whereby the strength and resistance to shock are increased and the moulding properties improved. Layers of textile fabric, impregnated with a solution of phenol-formaldehyde resin in volatile organic solvents, and moulded and hardened under heat and pressure, are used not only as insulating materials, but also for noiseless gears, bearings and decorative panelling. Wood, also, impregnated with the initial liquid material, and then heated, becomes coated with a hard enamel-like layer, equal to the best Japanese lacquer; and metal articles, similarly, can be covered with a hard and resistant coating.

For the production of plastics, use may be made not only of phenol but also of cresol, and besides formaldehyde other aldehydes may be employed. Thus, when phenol is allowed to react with an aldehyde known as furfuraldehyde (obtained by heating bran, corn-cobs, etc., with acid), another series of resins can be obtained, which, like bakelite, can also be used as plastic material.

By allowing butyraldehyde, $C_3H_7{\cdot}CHO$, to react with polymerized vinyl alcohol

$$(\ldots -CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2- \ldots),$$

a long-chain molecule is formed, one link of which can be represented by the formula



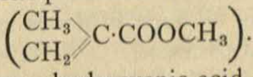
$$\begin{array}{ccccccc} -\mathrm{CH_2}- & \mathrm{CH} & - & \mathrm{CH_2} & - & \mathrm{CH} & -\mathrm{CH_2}- \\ & \cdot & & & & \cdot & \\ & \mathrm{O} & \text{——} & \mathrm{CH} & \text{——} & \mathrm{O} & \\ & & & \cdot & & & \\ & & & \mathrm{C_3H_7} & & & \end{array}$$

This forms a strong plastic material, polyvinyl butyral or *butvar*, used in the U.S.A. as an interlayer for triplex safety glass.

A notable advance in the production of synthetic plastics was made when it was discovered that a clear colourless solid is formed by the reaction between urea and formaldehyde. Attempts, however, to produce in this way an 'organic glass,' as a substitute for ordinary glass, failed, as it was not found possible to prevent the material from cracking under the strains brought about by shrinkage.

Fortunately it was found by the English chemist, E. C. ROSSITER, that when thiourea is substituted for urea, colourless resins are also produced; and by acting with formaldehyde on a mixture of urea and thiourea, under suitable conditions, a mixed thermosetting resin is obtained which has properties superior to either of the single resins, and which shows no tendency to crack. This mixed resin, produced industrially under the name *beetle ware*, forms a transparent, colourless material, of glass-like clearness. It may also be tinted or coloured and used for domestic ware, electric switches and fittings, lacquers and many other purposes.

Urea-formaldehyde resins are also made use of for the production of non-creasing cotton goods. The fabric is impregnated with a solution of urea and formaldehyde and the resin formed, by heating, on the fibre.

Of still greater importance as a transparent 'organic glass' is the synthetic resin introduced by Imperial Chemical Industries under the name *perspex*, a material produced from the compound known as methyl methacrylate  $\left(\begin{matrix}CH_3\\CH_2\end{matrix}\!>C\cdot COOCH_3\right)$. This compound—formed from acetone, hydrocyanic acid and methyl alcohol—is a liquid which, in presence of oxygen or organic peroxides, undergoes polymerization and is gradually transformed into a colourless glass.

Perspex (also called *lucite* in America) has a transparency second only to that of quartz glass and is the most successful organic substitute for glass so far obtained. It is thermoplastic and can be moulded into spectacle lenses, photographic lenses, and other optical apparatus.[1] The cost involved in grinding glass is thus avoided. As it is non-splinterable, perspex also finds extensive use in the construction of the cockpits, turrets, etc., of aeroplanes and in the production of bullet-proof 'glass.' Its specific gravity is only about one-third that of glass, but a sheet of perspex is about ten times as strong as glass of equal thickness. It is largely used for dentures and for making splints.

---

[1] The surface of perspex lenses may be protected against scratching by a thin coating of silica, deposited by high vacuum technique.

By allowing methyl methacrylate to undergo polymerization in an emulsified condition, the plastic is obtained in a granular form. This is sold for moulding purposes under the name *diakon*.

By means of a trace of oxygen, the unsaturated hydrocarbon ethylene, when under a high pressure, undergoes polymerization and forms polyethylene or *polythene*, a long-chain hydrocarbon consisting of about 1000–2000 CH_2– groups joined together. In this way one obtains a very remarkable plastic, one of the lightest of all the plastics and one which will float on water. It is characterized by toughness and flexibility, resistance to water, chemical inertness and unique properties as an insulator for electricity. Its discovery proved essential for the development of radar. Its tensile strength can be increased by cold drawing. It is used as a flexible insulating covering for electric wires and cables, for making squeeze bottles, collapsible tubes for creams and cosmetics, and for the production of flexible or rigid piping, which is, to some extent, replacing rubber and lead (Plates 33 and 34).

Polythene, produced in Britain under the name *alkathene*, is also used, in sheet form, for lining industrial containers and for wrapping all sorts of goods and materials, even machinery, for shipment overseas.

Related to polythene is the well-known and extensively used plastic, *polyvinyl chloride* (PVC), or polymerized vinyl chloride, $CH_2{:}CHCl$. This also is a very tough and water-resistant material and is used in plastic surgery, as an electric insulator, and for the manufacture of imitation leather and raincoats. It is also used for covering floors.

When all the four hydrogen atoms of ethylene are replaced by atoms of fluorine one obtains tetrafluoroethylene, $CF_2{:}CF_2$, This undergoes polymerization, similarly to ethylene, to form a chain of CF_2–groups and gives rise to the plastic *fluon* or *teflon*. It has great thermal and chemical stability and finds many uses in industry. In the realm of sport, also, it is found that skis coated with fluon are faster than untreated skis, because fluon is not wetted by the water film ordinarily formed and has an inherently low friction.

When ethylene is combined with benzene one obtains the compound styrene, $C_6H_5\cdot CH:CH_2$. This polymerizes to a glass-clear resin, polystyrene or *distrene*. It is a valuable thermoplastic resin which is finding widespread use for making wall tiles and all sorts of domestic ware.

In 1904, Professor F. S. KIPPING, of University College, Nottingham, synthesized a number of compounds of the types $R\cdot Si(OH)_3$, $R_2\cdot Si(OH)_2$, where R stands for a hydrocarbon radical such as $CH_3\cdot$, $C_2H_5\cdot$, etc. These compounds readily undergo condensation with loss of water and formation of substances of high molecular weight known as *silicones*. Since 1945 the production of silicones, which for long were of theoretical interest only, has been developed on an industrial scale, and a variety of silicones, liquid, semi-liquid and solid, have been produced, by a more direct process than that used by Kipping. They have very remarkable properties. Possessing great heat resistance and high electrical insulating properties, the silicones are used as heat-resisting varnishes; as insulating liquids in electrical transformers; as lubricants, the viscosity of which varies very little with the temperature, and as a rubber-like material which is stable to heat and is not hardened by cold. 'Bouncing putty' is a methyl silicone polymer which is extremely elastic to sudden impact and bounces like rubber when thrown against a hard surface, but is plastic and flows under gradually imposed pressure. The silicones are highly water-repelling and may be used to impregnate cotton and nylon to give a waterproof material. If sprayed on brick or concrete masonry, silicone prevents water from entering the pores of the masonry, but does not prevent the passage of air. Silicone is a powerful anti-foam agent.

RUBBER-LIKE MATERIALS

One of the most important materials in our present-day civilization is *rubber*, obtained by the coagulation, by means of acid, of the sap or latex of certain species of trees, more especially

Hevea brasiliensis. Although, formerly, rubber was obtained mainly from the 'wild' rubber trees, indigenous to the Amazon Valley, most of it is now derived from the plantations of cultivated trees in Malaya, Ceylon and Indonesia. The production of plantation rubber has been greatly improved and increased by scientific investigation.

The development of the rubber industry dates especially from the discovery, made in 1844 by THOMAS HANCOCK in London, that when rubber is 'masticated' by being disintegrated and worked between rollers, it forms a plastic mass, and from the later discovery that rubber can be vulcanized by means of sulphur or by treatment with certain compounds of sulphur. In this way the stickiness of rubber on being heated is counteracted. When the amount of sulphur taken up by the rubber amounts to about 50 per cent., a hard rubber known as *vulcanite* or *ebonite* is obtained. This is a material which had, at one time, a great vogue for the production of moulded articles.

Most of the rubber used at the present day for motor-car tyres and for rubber articles of all kinds is vulcanized, but the properties of the finished article can be greatly modified and the process of manufacture facilitated by the addition of different substances. In 1915, it was found that the addition of carbon black, for example, increases the tensile strength of the rubber and confers a high degree of resistance to abrasion. By the addition to rubber of about 28 per cent. of carbon black and of certain 'antioxidants,' whereby the tendency to crack on exposure to light and air is counteracted, the life of a motor-car tyre was trebled or quadrupled.

For many years chemists sought to produce artificially rubber or a rubber-like material, and in recent times great success has attended their efforts.

It has long been known that when natural rubber is decomposed by heat, the most important product is a hydrocarbon called *isoprene* ($CH_2{:}C(CH_3){\cdot}CH{:}CH_2$); and it was found that this compound, on being kept, very slowly undergoes polymerization to form a rubber-like material, consisting of a large number of isoprene molecules combined together to form a large complex molecule. The process of polymerization, however, took place so slowly that it was industrially of no value. In 1910, the important discovery was made, first in England and then in

Germany, that the polymerization of isoprene is very greatly accelerated by metallic sodium.

Although the polymerized isoprene was of no practical significance, it was found that the simpler hydrocarbon *butadiene* ($CH_2{:}CH{\cdot}CH{:}CH_2$) can also be caused to polymerize with the formation of a rubber-like material; and it is on the development of this process, more especially, that the efforts of chemists, at first in Germany but in more recent years in the U.S.A., Canada, Russia and in England, have been concentrated. The artificial rubber produced from butadiene is generally referred to as *Buna*.[1] The butadiene required for this process can be synthesized from acetylene, and it is also obtained by various processes from alcohol and from the gases butane and butylene which are present in or can be obtained from petroleum. To bring about the polymerization of butadiene, other catalysts than sodium, *e.g.* potassium persulphate, are now also used.

To improve the qualities of the butadiene rubber, the butadiene is generally mixed with another polymerizable substance, especially with styrene, $C_6H_5{\cdot}CH{:}CH_2$, or with acrylic nitrile, $CH_2{:}CH{\cdot}CN$, and the two substances are polymerized together. The products so obtained are known as *Buna S* (renamed, in the U.S.A., GR.S[2]) and *Buna N*.

At an earlier date, the firm of du Pont de Nemours introduced another synthetic rubber-like material, *neoprene* (or *duprene*), formed by the polymerization of chlorinated butadiene or *chloroprene* ($CH_2{:}CCl{\cdot}CH{:}CH_2$). Although more similar to rubber in its molecular constitution than are other synthetic products, neoprene should not be regarded merely as a rubber substitute. It should rather be regarded as a new material with its own special qualities which make it suitable for a great variety of purposes for which rubber is not so well adapted. Neoprene, while it equals rubber in elasticity, strength and resistance to abrasion, is greatly superior to rubber in its resistance to petrol, oils, fats, solvents, heat and ozone. It is also less pervious to gases. While it can be destroyed by heat, it does not propagate flame. For many purposes, therefore, neoprene should be used in preference to rubber.

By treatment with chlorine, rubber can be chlorinated, and chlorinated rubber is now produced under the name *alloprene.* Mixed with a suitable solvent (*e.g.* xylene), with addition of decalin (decahydronaphthalene) or of solvent naphtha, according to the rate of drying required, and with a plasticizer (*e.g. cerechlor* or chlorinated paraffin wax), alloprene is used as a protective paint, highly resistant to acids, alkalis and salts. In a fibrous or spongy form, alloprene is also an excellent heat and sound insulator. It can readily be moulded when hot.

---

[1] The name Buna is derived from bu(tadiene) and Na, the symbol for sodium.

[2] That is, Government Rubber-Styrene.

Chapter 15

FERMENTATION AND THE ACTION OF ENZYMES AND MICRO-ORGANISMS

WE have already seen how Nature, in carrying out her wonderful syntheses and decompositions within the animal and plant organism, makes use of a number of catalysts, the so-called *enzymes*, produced within the cells of the living plant or animal. Even in the lowliest forms of life, when as yet differentiation of structure and function has not appeared, when life with all its mystery is contained in the microcosm of a single cell, even there also these complex catalysts, without whose presence the great life-processes would slow down to the sluggishness of death, are produced, and exercise their quickening power. Borne on the breeze, carried in water, the earth teeming with their countless myriads, these micro-organisms—the yeasts, bacteria and moulds—through the enzymes which they produce, carry out, unseen, the never-ceasing changes of an ever-changing Nature. Putrefaction and decay, by means of which Nature resolves the body of a life outlived into the elements from which new living structures can be built; the souring and curdling of milk; the production of the dyestuff indigo from the compound indican contained in the woad; the 'puering' of hides and the curing of tobacco; the development of the pungent flavour of mustard and the production of benzaldehyde or oil of bitter almonds from the amygdalin contained in the almond seed; all these and many other processes—so-called fermentation processes—by which complex organic material is broken down into simpler substances, are brought about by the action of living organisms which secrete the enzyme-catalyst appropriate to the process.

This explanation of the fermentation process—a term at first applied to all changes which are accompanied by effervescence due to the escape of gas—is one which has been accepted by science only in comparatively recent years.[1] Prior to 1857, chemists and biologists were divided in their views. Some favoured the physical and chemical explanations put forward by Berzelius and Liebig. The former, who introduced the conception of 'catalytic force,' likened fermentation to the decomposition of hydrogen peroxide under the influence of platinum; and the latter, with greater apparent definiteness, regarded a ferment as being an unstable substance which, formed by the action of oxygen on the nitrogenous materials of the fermentable liquid, undergoes a decomposition. The internal motion which thereby took place was regarded as being communicated to the fermentable medium. With these mechanical explanations, however, dissatisfaction became more and more widely expressed, and in 1857 it was shown conclusively by Pasteur, to whose genius the advance of science in many directions is due, that all fermentative changes are associated with and produced by living organisms; and this vitalistic explanation, summed up by Pasteur in the well-known phrase, 'No fermentation without life,' is accepted, in the main, at the present day. The growth of knowledge, however, has rendered necessary a certain modification of the views which were put forward in the middle of last century.

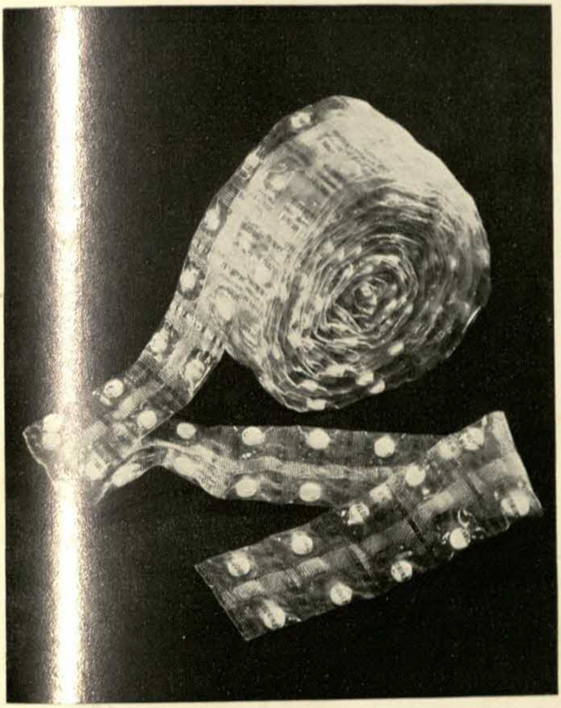
---

[1] The term fermentation is now applied to changes brought about by micro-organisms. Evolution of gas is not an essential criterion.

For a considerable time the view was held that the fermentation processes are the result of the direct action of the living organism on the fermentable material. Cases, however, began to accumulate of changes brought about by substances, *e.g.* diastase and pepsin, which are the product, certainly, of life, but are not themselves living; and the matter was put beyond dispute in 1897 when E. BUCHNER showed that in the production of alcohol from sugar, the fermentation is brought about not by the direct action of the living organism, but by a substance, which he called *zymase*, produced by and contained in the cell of the yeast.[1] It is now generally accepted, therefore, that fermentation changes are produced by substances which although produced by living organisms are not themselves living; and to these substances the name *enzyme* (Greek *en zymē*, in yeast), introduced in 1878, is applied. In proposing the adoption of this term, the German physiologist, W. KÜHNE, stated: 'This is not intended to imply any particular hypothesis, but it merely states that *en zymē* (in

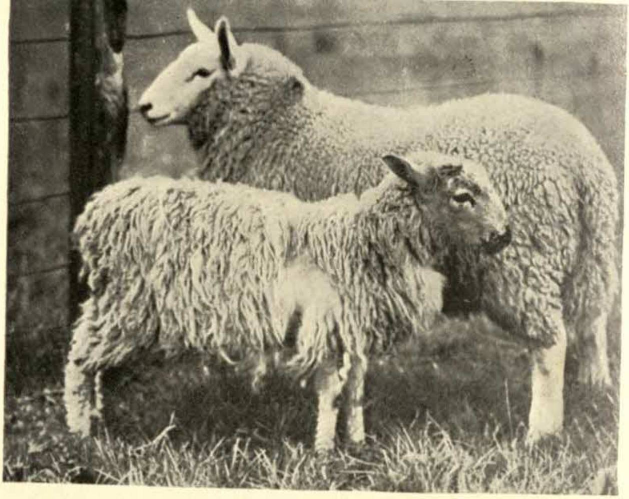
---

[1] The enzyme, zymase, is associated in the yeast cell with another substance called a co-enzyme. The presence of both enzyme and co-enzyme is necessary for fermentation.



33. TABLETS OF PALUDRINE IN ALKATHENE ENVELOPES

34. POLYTHENE SQUEEZE-BOTTLE

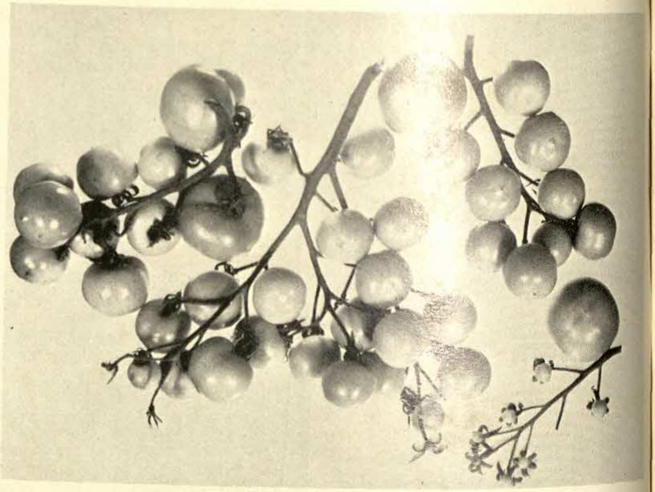


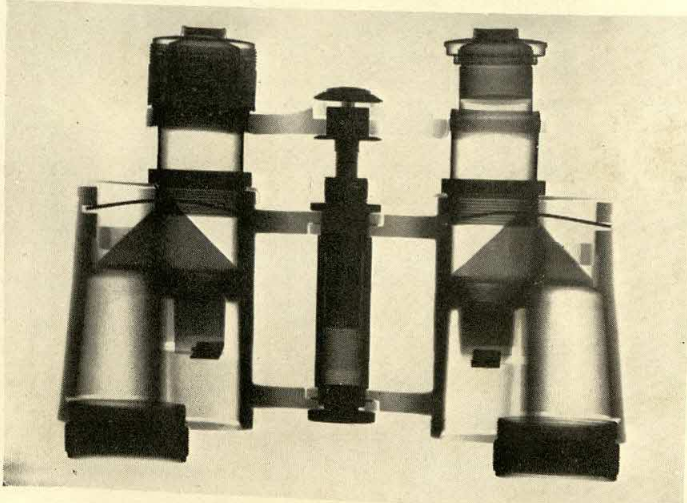
35. 'PINE' DISEASE IN LAMBS

Two lambs of the same age—the front one suffering from the disease known as 'pine' due to cobalt deficiency

36. PARTHENOCARPY IN TOMATOES

Trusses treated with NoXD. The truss at the bottom right-hand corner was untreated





37. PHOTOGRAPH OF BINOCULARS BY GAMMA RAYS

yeast) something occurs that exerts this or that activity, which is considered to belong to the class called fermentative. The name is . . . intended to imply that more complex organisms, from which the enzymes, pepsin, trypsin, etc., can be obtained, are not so fundamentally different from the unicellular organisms as some people would have us believe.'

Not only do the enzymes play an indispensable role in the economy of Nature, but they play also an essential part in many of the most important industrial processes. Of the processes which depend on fermentation, none is of greater importance than that which has been carried on from the earliest days of man's history, the fermentation of sugar with production of alcohol.

Although in chemistry the term 'alcohol' is a generic one, and is applied to a whole series of compounds in which the so-called *hydroxyl* group (OH) is present, the name when used without qualification is applied to the best known and most valuable of the alcohols, *ethyl alcohol* ($C_2H_5{\cdot}OH$), or as it is frequently called, *spirits of wine*. In the fermentation industry, it is sometimes also called grain spirit or grain alcohol, or potato spirit, according as the raw material of its manufacture is derived from grain or from potatoes.

Alcohol is produced by the action of a particular enzyme, zymase, on certain sugars, the most important of which is the sugar glucose which, along with the isomeric sugar, fructose, is found in sweet fruits and in honey. Zymase is secreted by the micro-organisms known as yeasts (*Saccharomycetes*), and when yeast is introduced into a solution of glucose, decomposition of the latter with production of alcohol and of carbon dioxide is brought about through the agency of the zymase. Not all sugars, however, can be fermented by zymase. Thus, cane or beetroot sugar (known chemically as *sucrose*), and malt sugar or maltose, are not fermentable with zymase. If, however, yeast is introduced into solutions of these sugars, fermentation does take place, owing to the fact that yeast secretes not only the enzyme zymase, but also the enzymes *invertase* and *maltase*. The former of these converts cane and beetroot sugar into the two simpler isomeric sugars, glucose and fructose, by a process of hydrolysis,

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

and maltase, similarly, converts maltose into glucose. The production of alcohol from sugars by means of yeast is, therefore, to be referred, in the last instance, to a fermentation of glucose (sometimes also of fructose) by zymase.

Fermentable sugars can be obtained not only from sucrose (which is largely employed in France in the form of beetroot molasses), but also from starch, which constitutes, as a matter of fact, by far the most important raw material for the manufacture of alcohol. The starch is of varied origin. In England it is derived mainly from maize, rice, wheat and barley, and in the United States, also, maize (corn) is largely used. In Germany, most of the starch is derived from potatoes.

For the conversion of the starch into fermentable sugar, use is chiefly made of the enzyme *diastase*, contained in malt; or, the starch can also be converted into glucose by heating with dilute sulphuric acid. In the latter process, the large starch molecule undergoes hydrolysis and breaks up into the smaller molecules of glucose of which, like the cellulose molecule, it is built up. It is of some interest to note here that the reverse process, the synthesis or building up of the starch molecule by the condensation of molecules of glucose, has also been effected under the influence of enzymes.

For the production of malt, barley grains are steeped for some days in water and then spread out, or 'couched,' to a depth of two or three feet on the floor of the malt-house. Soon the moist grain begins to sprout and to become hot. As the temperature must not be allowed to rise above 15° C. or 60° F., the 'couch' is broken down and the germinating barley spread out in a thin layer, only a few inches in depth, turned over from time to time so as to allow access of air to the grains, and sprinkled with water when necessary. During the germination of the barley, diastase and other enzymes are produced, and when growth has proceeded sufficiently far, it is stopped by allowing the rootlets to wither, and then drying the malt in a kiln. The malt, which contains a considerable amount of starch and a small amount of sugar, together with the enzyme diastase, is crushed and mixed with hot water, and a quantity of raw grain or potato starch is added. By the action of the diastase, which is best carried out at a temperature between 40° and 60° C. or 104° and 140° F., the starch is converted into maltose or malt sugar. When this process of 'mashing' is complete, the liquid is boiled to destroy the diastase, and the sweet liquor or 'wort' is run into the fermenting vats and yeast is added.[1] By the action of the enzyme maltase, which is contained in the yeast, the maltose is converted into glucose; and this in turn is converted by the yeast-enzyme zymase mainly into alcohol and carbon dioxide, although small quantities of other substances—higher alcohols, succinic acid, glycerine, etc.—are also produced.

Alcohol may also be produced by the action of yeast on commercial glucose—obtained by heating starch (*e.g.* potato starch), or cellulose, with dilute sulphuric acid—or on cane sugar and beetroot sugar molasses (sucrose). In the latter case, conversion of the sucrose to the fermentable sugars, glucose and fructose, is effected by the yeast-enzyme invertase.

When fermentation is allowed to take place at a temperature of about 15° C. or 60° F., a turbulent effervescence is produced and the evolution of carbon dioxide is so rapid that the yeast cells are carried to the surface of the liquid and there form a thick froth. This is known as 'top fermentation,' and is the process which is mostly used in England. On the other hand, when the temperature is kept low, say about 6° C. or 43° F., the evolution of carbon dioxide is too slow to buoy up the yeast cells, and these, therefore, remain at the bottom of the vat. This is known as 'bottom fermentation,' and is made use of in Germany in the production of certain beers.

The fermentation of the sugar solutions does not proceed indefinitely, and when the liquid contains from 10 to 18 per cent. of ethyl alcohol, the fermentation stops. The liquid, or 'wash,' as it is now called, contains not only ethyl alcohol, but also furfural (or furfuraldehyde) and fusel oil—a mixture of higher-boiling alcohols, such as butyl alcohol, $C_4H_9{\cdot}OH$, and amyl alcohol, $C_5H_{11}{\cdot}OH$, and other substances. From these different substances the ethyl alcohol is separated by distillation in special fractionating stills, from which a mixture of alcohol and water containing about 96 or 98 per cent. of alcohol by volume is directly obtained. Alcohol so obtained is spoken of as 'silent spirit,' or 'patent still spirit.' By allowing this alcohol to stand over quicklime for some time and then distilling, 'absolute alcohol,' or pure ethyl alcohol, is obtained.[1]

---

[1] The necessity for using pure culture yeasts belonging to definite races is now recognized. The result of the fermentation varies with different yeasts.

For industrial and other purposes, alcohol finds abundant and varied use. Not only is it employed as a heating agent, in spirit lamps, but it is also used, to some extent, as an illuminant (with incandescent mantles), and as a motor fuel, when mixed with ether or with benzene. Its relatively high cost, however, militates against any immediate and extensive development in this direction. Alcohol is also used very extensively as a solvent in the preparation of varnishes, lacquers and enamels;[2] in the manufacture of ether, chloroform, acetic acid, celluloid, collodion, dyes, cordite and similar explosives, and many other substances. Ordinary *methylated spirit*, so largely used in spirit lamps and for other purposes, consists of ethyl alcohol 'denatured' by the addition of wood-naphtha (crude wood spirit or methyl alcohol), and mineral naphtha, the presence of which is intended to render the liquid undrinkable. Such methylated spirit is free from the excise duty ordinarily placed on alcohol. For industrial purposes, special *industrial methylated spirit* can also be obtained which consists of alcohol denatured with wood-naphtha only or with other denaturants suitable for particular industries.

In the process already described, starch is converted into fermentable sugars by means of diastase or by heating with dilute sulphuric acid. About the beginning of this century, however, another process, the so-called 'amylo' process, was introduced for the saccharification of starch, and this process has now developed into an industry of considerable magnitude.

Many moulds produce the enzyme diastase and possess, therefore, the power of converting starch into fermentable sugar. This fact has been made use of in the East from very early times, Chinese yeast, which has been largely used for this purpose, containing the mould *Mucor rouxii*. Mixed with various materials, it is sold under the name of 'migen' or 'men.' In the modern process, which has been carried out chiefly in France, and to a less extent in Spain, Italy and the United States, the moulds employed are *Rhizopus delemar* and *Mucor boulard*.

---

[1] For the purposes of taxation in Great Britain the strength or concentration of a spirit is generally expressed in terms of 'proof' spirit. Proof spirit is a mixture containing 49·24 per cent. by weight, or 57·1 per cent. by volume, of alcohol. Weaker spirits are said to be so much 'under proof' according to the percentage of water and proof spirit which they contain. Thus, a spirit 10° under proof means a liquid which contains, at 60° F., 10 volumes of water and 90 volumes of proof spirit. 'Over-proof' spirits are defined by the number of volumes of proof spirit which 100 volumes of the spirit would give when diluted with water to proof strength. If 100 volumes of an over-proof spirit would yield 150 volumes of proof spirit, it is said to be 50° over proof.

[2] For many technical purposes the place of ethyl alcohol is being taken by the cheaper isopropyl alcohol ($CH_3{\cdot}CH{\cdot}OH{\cdot}CH_3$), which is prepared synthetically by passing acetone vapour and hydrogen over a heated nickel catalyst, or by the action of dilute sulphuric acid, in presence of a catalyst, on propylene obtained by the cracking of mineral oils.

Maize, rice, potatoes, or other starchy material is reduced to a state of fine division and then steeped for a short time in water; after this, it is heated by means of steam so as to render the starch gelatinous. The liquid ('mash') is transferred to the fermenting vessel and after it has cooled down, spores of the mould are added. Growth takes place rapidly, and in twelve or fifteen hours the mass is penetrated by the mycelium of the mould. A few hours after the introduction of the mould, when a certain amount of sugar has been formed, yeast is added; the processes of saccharification and of fermentation then go on side by side. Less fusel oil is produced in this process and the yield of alcohol is higher than when the fermentation is carried out in the ordinary way.

Although ethyl alcohol is produced mainly by the fermentation process, large quantities are also produced in Switzerland from acetylene,[1] and it can readily be manufactured, also, from the hydrocarbon ethylene, enormous quantities of which are available from the cracking of mineral oils.

In the case of *alcoholic beverages*, although ethyl alcohol is the most important ingredient, the taste, aroma and special character of each depend on the presence of small quantities of other substances, which vary both in amount and in kind with the materials from which the beverage is prepared, and with the method of its preparation. These beverages may be classed into distilled liquors (spirits), wines and beers.

In the case of *whisky*, the process of fermentation is carried out essentially as already described; malted barley, mainly, is employed, and the wash is distilled from a simple pot-still similar to that shown in Fig. 27. The result, therefore, is no merely a mixture of pure alcohol and water, but one which also contains small quantities of various other substances—fusel oil, aldehydes, esters, etc. This raw whisky is then placed in casks to mature, and during this process the aldehydes become converted into acids which unite with the alcohols present to form esters. These give a special flavour and aroma to the whisky.

---

[1] Since acetylene can be produced from methane (p. 69), the production of alcohol from acetylene can profitably be carried out in countries, such as Italy, in which an adequate supply of natural gas is available.

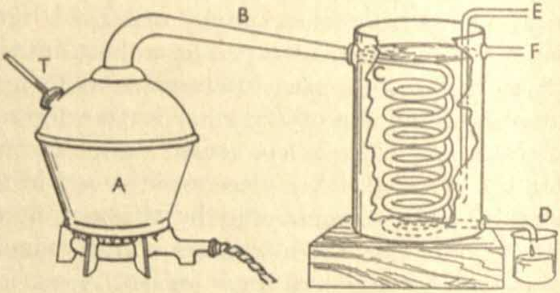


FIG. 27.—APPARATUS USED FOR DISTILLING LIQUIDS

A, a vessel in which the liquid is boiled and so converted into vapour which passes through the long neck, B, to a spiral "worm," or condenser, C, kept cold by means of flowing water. The condensed vapour issues at D and can be collected. E, tube through which cold water enters; F, exit for warm condenser water; T, thermometer to indicate the temperature of the vapour.

In the case of *gin*, the distilled spirit is flavoured by re-distilling with juniper berries, coriander, fennel, or other substances; *brandy* is obtained by distilling wine, and owes its particular flavour to the various esters contained in the wine from which it is prepared; and *rum*, prepared from fermented molasses, owes its flavour chiefly to the esters, ethyl acetate and ethyl butyrate. Sometimes it is also flavoured by placing the leaves of the sugar-cane in the still.

These distilled liquors all contain a high percentage, 40 to 50 per cent. or more, of alcohol.

Wines are prepared by the fermentation of fruit juices—chiefly juice of the grape—in which the two sugars, glucose and fructose, are present. The juice also contains various acids, especially tartaric acid; and the skins of the grape contain tannin, various essential oils, and, it may be, colouring matter. These all pass into the juice when the grapes are pressed, and according to their nature and relative amounts, give wines of different flavours and qualities.

Owing to the presence of a species of *Saccharomyces* on the grape itself, fermentation of grape juice must have been observed in warm, grape-growing countries at a very early period in man's history; and the manufacture of wine must have been developed at a very remote time. Although the grapes are now crushed mainly by wooden rollers, the method of treading with the bare feet—treading the wine press—has not yet ceased to be practised. The juice extracted from the grape is called 'must,' and by its fermentation, alcohol is produced. After the first 'active fermentation' is over, the 'new wine' is drawn into casks which are filled full and loosely closed in order to prevent the conversion of the alcohol into acetic acid (p. 265). In the casks, a 'still fermentation' proceeds for several months, during which time the yeast settles down, and the tartaric acid, along with various salts and colouring matters, separates out as *argol.* This consists chiefly of potassium hydrogen tartrate, and is the main source of this salt, known familiarly as *cream of tartar.*

After the wine has become clear, it is drawn off into casks and allowed to ripen for perhaps two or three years. During this process, the tannin and some other impurities are precipitated, and at the same time the alcohol and fusel oil combine with the small quantities of acids present to form esters, which give the peculiar and characteristic flavour and 'bouquet' to the wine. After ripening, the wine is bottled.

Since the quality of the grape juice varies with the soil, and also with the climate, some vintages give better wines than others. Wines, also, are subject to 'diseases,' due to the presence of enzymes, which bring about an alteration of the wine, *e.g.* conversion of alcohol into acetic acid.

For the production of *beers,* malted grain is employed, but in the mashing process the complete conversion of the starch into maltose is not allowed to take place, a portion being converted only into the intermediate product of hydrolysis, dextrin.[1] This dextrin is retained in order to give 'body' to the beer. Further, the nitrogenous compounds, the albuminoids and proteins, in the grain are converted by the malt-enzyme, *peptase*, into peptones and other substances, which also add 'body' to and increase the nutritive properties of the beer. All these various substances are classed together under the name 'extract.'

---

[1] Dextrin is also produced industrially by heating starch with dilute sulphuric acid. It is used as an adhesive on stamps, envelopes, etc. It constitutes the so-called 'British gum.'

When mashing is complete, the wort is drawn off and boiled with hops, and, after settling, the clear liquid is fermented with yeast. When the active fermentation has subsided, the new beer is run into casks and slow fermentation allowed to continue, the froth which is formed being allowed to pass out through the bung-hole. At the conclusion of the process, the beer is drawn off into casks or bottles.

The fusel oils obtained as by-products in the manufacture of ethyl alcohol, and formerly regarded as waste material, are now subjected to special distillation in order to obtain the higher alcohols present. Although the composition of the fusel oil depends on the process in which it is formed, one can obtain from the different fusel oils the alcohols known as propyl alcohol ($C_3H_7{\cdot}OH$), butyl and iso-butyl alcohol ($C_4H_9{\cdot}OH$), and amyl and iso-amyl alcohol ($C_5H_{11}{\cdot}OH$). These alcohols find their use not only in the scientific laboratory, but also in industry, for the purpose of preparing artificial fruit-essences, and as solvents. These artificial fruit-essences and flavouring materials are pleasant-smelling compounds of alcohols with acids, known as *esters*.[1] Thus amyl acetate (from amyl alcohol and acetic acid) forms the main constitutent of artificial essence of pears; ethyl butyrate (from ethyl alcohol and butyric acid) is used in making artificial essence of pineapples; amyl butyrate is used in making apricot essence; and amyl iso-valerate (from amyl alcohol and iso-valeric acid) is used as a constituent of apple essence.

The introduction and increasing use of nitro-cellulose lacquers, and the need for special solvents and plasticizers, have led to a demand for butyl and amyl alcohols which is greater than can be satisfied by fusel oil. Chemists, therefore, have been called upon to develop processes for the large-scale manufacture of these alcohols and of esters derived from them. At the present day, butyl alcohol (or butanol) is produced industrially from a

[1] Esters are formed by the combination of alcohols and acids with elimination of water, *e.g.* $CH_3{\cdot}COOH + HO{\cdot}C_2H_5 = CH_3{\cdot}CO{\cdot}OC_2H_5 + H_2O$.

mixture of carbon monoxide and hydrogen (p. 122), from acetylene, and by the fermentation of starch (from maize, for example), by means of an organism, *Clostridium acetobutylicum*. In this process there are produced butyl alcohol (about 60 per cent.), acetone (about 30 per cent.), and ethyl alcohol (about 10 per cent.), as well as large quantities of carbon dioxide and hydrogen. The carbon dioxide is liquefied and then converted into carbon dioxide snow, while the hydrogen is used for the production of ammonia. From butyl alcohol there are produced various compounds, *e.g.* the solvent, butyl acetate, and the plasticizer, butyl phthalate (from butyl alcohol and phthalic acid). Acetone, also, is a valuable solvent and is used in the manufacture of cordite, etc. Amyl alcohol is now produced industrially from the hydrocarbon pentane, C_5H_{12}, large quantities of which are present in natural gas.

Many weak alcoholic beverages, such as light wines, become sour when exposed for some time to the air. This souring is due to the conversion (oxidation) of the alcohol to acetic acid by the oxygen of the air, under the influence of certain fungi and bacteria (*e.g. Mycoderma aceti* and *Bacterium aceti*); and the process is carried out on a large scale for the production of *vinegar*.

In England, vinegar is manufactured mainly from malt, which is mashed and fermented with yeast as in the preparation of alcohol. After fermentation, the alcoholic liquor (in which not more than 10 per cent. of alcohol should be present), containing the nitrogenous matter and salts necessary for the growth of the bacteria, is sprinkled over beechwood shavings or basket-work inoculated with the acetic acid bacteria, and contained in a large vat to which air can be admitted. In this way the alcoholic liquor is spread over a large surface while exposed to the action of the air, and oxidation of the alcohol to acetic acid rapidly takes place. The liquid is drawn off from the bottom of the vat and passed repeatedly over the same shavings or basket-work, until conversion of the alcohol to acid is nearly complete. A very small amount of alcohol, however, is left in the vinegar because, otherwise, oxidation and destruction of the acetic acid would take place.

Vinegar thus obtained contains about 6 per cent. of acetic acid, but commercial vinegars are frequently weaker. Vinegar is also frequently made, especially in France, from wines, the process being carried out, as a rule, in large casks.

Although vinegar is, essentially, a dilute solution of acetic acid in water, it receives its special flavour and quality from the presence of small quantities of other substances derived from the materials of its preparation, malt, wine, etc. More especially does it contain esters, like ethyl acetate, which impart their aroma to the vinegar.

Sometimes 'vinegars' are prepared artificially by adding to a solution of acetic acid in water, caramel or burnt sugar, and various aromatic substances and esters.

The production of acetic acid on an industrial scale is not carried out by the method just described, since only a dilute solution (up to 10 per cent.) can be obtained in this way, but, as we have seen, by the distillation of wood. The pure acid forms ice-like crystals, which melt at 17° C. (62·6° F.), and is spoken of as *glacial acetic acid.*

Since, owing to the synthetic production of methanol from carbon monoxide and hydrogen, the wood distillation industry has greatly diminished, other methods have come into prominence for the production of acetic acid. When acetylene is passed into a dilute sulphuric acid solution containing mercuric sulphate, which acts as a catalyst, the acetylene combines with water to form a compound known as *acetaldehyde* ($CH_3{\cdot}CHO$). Acetaldehyde is also produced industrially by passing the vapour of ethyl alcohol over heated silver-gauze. Under the catalytic action of the silver, hydrogen is removed from the ethyl alcohol and acetaldehyde is formed. By passing air or oxygen into liquid acetaldehyde to which solid manganese acetate has been added, oxidation of the aldehyde to acetic acid ($CH_3{\cdot}COOH$) readily takes place. By acting on acetaldehyde with hydrogen in presence of nickel, as catalyst, the aldehyde is reduced to ethyl alcohol, $CH_3{\cdot}CH_2{\cdot}OH$.

At a low temperature, in presence of acids, acetaldehyde undergoes polymerization and forms a white solid, known as *metaldehyde.* This is used as a 'solid fuel,' in place of methylated spirit, under the name 'Meta.'

The solvent *acetone,* to which repeated reference has been made, is produced not only by the fermentation process already described, but also by passing the vapour of acetic acid, at a temperature of about 400° C. (752° F.), over a catalyst, *e.g.* oxide of thorium or of manganese. It is also produced by passing ethyl alcohol and steam over a suitable catalyst; by passing the vapour of isopropyl alcohol (p. 260, footnote) over a copper catalyst at 500° C.; or by passing a mixture of acetylene and steam over a heated zinc oxide-iron catalyst. These processes afford further illustration of the importance of catalysis, on which emphasis has already been laid.

When rennet is added to milk, the enzyme *rennin*, which it contains, brings about a curdling of the milk by causing a decomposition of the casein present in the milk into para-casein which forms the curd, and whey albumin. This process of enzyme action is one of great importance, because it is employed not only for the industrial production of casein, but also as the first step in the manufacture of cheese. In making *cheese*, a 'starter,' or culture of bacteria capable of producing lactic acid from milk-sugar is added to milk at a controlled temperature, and rennet is then added. By careful control of the temperature and of the acidity, which increases gradually, owing to the production of lactic acid, casein separates out as a curd, from which, later, whey is expelled. After allowing the curd to remain for some time in order to mature, it is ground, salted and pressed in a cheese-mould. The cheese is then allowed to 'ripen,' when a complicated series of changes takes place under the influence of various enzymes, part of the casein undergoing a decomposition, with production of a number of different substances, the nature and amount of which vary greatly in the different kinds of cheese. The presence of these decomposition products gives the characteristic flavour to the cheese. The different kinds of cheese vary considerably in composition, but contain about 24 to 40 per cent. of water, 23 to 39 per cent. of fat, 27 to 33 per cent. of casein and other nitrogenous compounds, and 3 to 7 per cent. of salts.

In the industrial production of casein, skimmed milk is used, and the milk may be curdled by means of rennet, as described already, or by the addition of hydrochloric acid with careful control of the acidity. This acid-produced casein has a different composition and different physical properties from that obtained with rennet. It is largely used as a sizing material for paper and cotton; in calico printing; and in the manufacture of casein water-paints or *distempers* (casein mixed with alkali and slaked lime, to which mineral colouring matters are added).

Reference has been made to the fact that in the production of alcohol by fermentation glycerine is formed as a by-product. Normally, the amount of glycerine is small, but by modifying the conditions under which fermentation takes place, by making the liquid slightly alkaline, for example, by addition of sodium sulphite or sodium carbonate, the yield of glycerine can be greatly increased. Although under present conditions the process may not compete economically with the saponification of fats, it may be that in the future the fermentation process will be able, at least, to hold its own and so contribute to the conservation of important foodstuffs.

In recent years the importance of micro-biological processes has become more fully recognized, and their industrial applications have been extended. For the production of antibiotics, for example, we are dependent almost entirely on biosynthetic processes; and the micro-biological production of lactic acid, citric acid and certain vitamins (*Chap.* 16) is carried out industrially on a large scale. More recently, bacterial activity has been made use of for the production of *dextran*, a polymer of glucose, which is used therapeutically and as a serum substitute or 'expander,' to maintain the circulating blood volume in cases of shock. In other directions, also, increasing use will no doubt be made of the rapid growth and synthesizing power of micro-organisms.

Chapter 16

VITAMINS AND HORMONES

THE fundamental problem of organic chemistry, according to the French chemist, MARCELIN BERTHELOT, was the investigation of the compounds occurring in plants and animals and the proof 'beyond all question that compounds identical with those produced by plants and animals can be synthesized from inorganic or mineral matter.' This, no doubt, is somewhat too narrow a view to take of the aims and objects of organic chemistry, but the interest of such investigations made a powerful appeal to some of the foremost organic chemists in the second half of the nineteenth century, and led to the elucidation of the constitution and, in some cases, to the synthesis of sugars, essential oils, proteins and other products of the animal or plant organism. During the present century, interest in the compounds produced in plants and animals has been revived, and through the investigations of such substances there has been built up the important and rapidly growing branch of science known as *biochemistry*. One of the most notable features of this development has been the close co-operation which has been established between the organic chemist and the physiologist in the investigation of the processes of human nutrition and of the factors involved in the maintenance of health. It is possible to consider here only a few of the more important discoveries which have resulted from this co-operation.

In these days when so much interest is being taken in the health of the people and in the attainment of physical fitness, it can be no matter for surprise—it is, in fact, most desirable—that, especially in days of food scarcity, the subject of nutrition should arouse the widespread interest not only of those responsible for government and administration but also of the people as a whole; for health depends on adequate and proper nourishment, and without good health there can be no physical fitness.

Until early in this century, the problem of nutrition seemed to be a comparatively simple one and to find its solution in the supply to each individual of a sufficient amount of the proteins, fats and carbohydrates, together with salts and water, necessary to build up the tissues of the growing body, to repair waste, and to supply the energy necessary for the maintenance of the body temperature and the performance of mechanical work. It was the fear that the supply of food might become inadequate in amount that oppressed Sir William Crookes in 1898 (p. 129), and it was the prospect of famine that stimulated the increased production and use of fertilizers. That fear has, to a great extent, been removed and agricultural chemists have shown how the problem of producing an adequate supply of food to feed the world's growing population can be solved. At the present day, interest is centred not so much in the quantity of food as in the quality; not in the amount but in the kind. A sufficiency of proteins, fats and carbohydrates is, of course, still essential, but the danger to health comes, except in times of special crisis, not so much from under-feeding, although that is not everywhere absent, as from wrong feeding.

Before the recent discoveries in the science of nutrition had been made, food was thought of mainly as a fuel, and the adequacy of a diet was decided largely on the basis of its fuel value, the amount of energy or the number of calories (p. 46) to which it could give rise by its combustion in the body. In the absence of fuller and more exact knowledge, one had to be content, more or less, with this view, although its inadequacy had been demonstrated by medical experience. It had long been known, for example, that one of the most distressing and fatal diseases to which sailors absent from home on long voyages were subject was scurvy, a disease affecting not only the skin but the whole system, and which, if not checked, must end fatally. Even on land, thousands have died of this disease and, during the Great War of 1914–1918, it attacked the Indian soldiers in Mesopotamia (Iraq). And yet, early in the eighteenth century, it had been shown that this disease could be cured by the administration of lemon or orange juice.[1] No drugs, in the ordinary sense, were necessary; only a slight alteration of the diet. Many found it difficult to believe that such a dreadful disease could be cured by such easy means. In a similar manner it gradually came to be realized that other diseases, *e.g.* beri-beri and rickets, could be cured by dietary measures. In other words, it came to be realized that these diseases are due not to the presence of toxins or other harmful substances in the diet or produced in the body, but to the absence of certain essential substances from the diet.

---

[1] Even in the seventeenth century, lemons and oranges were used for the cure of scurvy among the crews on the ships of the East India Company.

It was, more especially, by the work of Sir F. GOWLAND HOPKINS, at Cambridge, in 1906, and, later, of Professor MCCOLLUM and Miss MARGUERITE DAVIS, in America, that definite proof was obtained that health cannot be maintained on a diet of protein, fat, carbohydrate and salts only, but that small quantities, sometimes very minute quantities, of other substances, which were given the general name of *vitamins*, are necessary. By the application of this new knowledge, results, sometimes of a spectacular character, have been obtained in the prevention and cure of a number of diseases, the cause of which had long been obscure. It has also come to be realized that there may be a wide gap between perfect health and obvious disease; and that, even when there is no obvious disease, improvement of health, vigour and enjoyment of life may be brought about by an increase of the vitamins in the diet. It is now also realized that minor ailments, carious teeth, slight rickets, gastric disturbances, etc., may be the result of mistakes in feeding and lack of vitamins. For this reason, greater attention is now also being given to improving the quality or vitamin content of foodstuffs, a matter which is of especial importance in these days of a more sophisticated civilization, when so much of our food is 'processed' and thereby sometimes rendered deficient in vitamins.

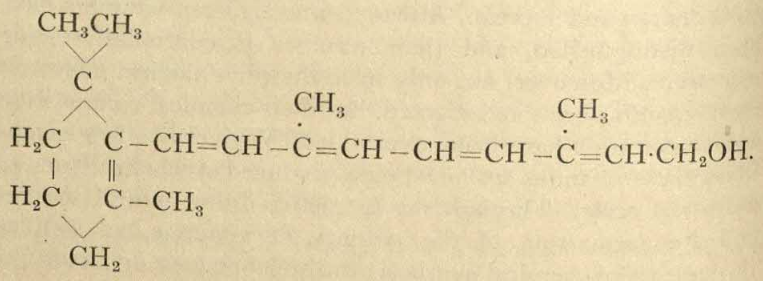
The discovery of the existence and importance of vitamins initiated a search for and an investigation into the sources and nature of these 'accessory food factors,' as they were first called; and this investigation has been and is being carried out with great energy and success. Already some eighteen vitamins have been distinguished, and their number is continually being increased. Moreover, not only have the physiological effects of these vitamins been investigated, but their chemical composition and constitution have been ascertained. With only a few exceptions, these vitamins are now being produced synthetically on an industrial scale. Through the extraction from natural sources and standardization of the potency of vitamins, as well as through their chemical synthesis in the laboratory or factory, it is now possible to enrich foods, when so desired, with vitamins in definite and controlled amount.

With regard to the chemical action and function of vitamins it has been found that vitamins are either co-enzymes (p. 256), in the absence of which the enzymes necessary for carrying on the various life processes cannot act, or are constituents of co-enzymes.

Ignorance of the nature and chemical individuality of the vitamins, when first discovered, led to their being designated by the letters of the alphabet, and this nomenclature is still to some extent retained. Some of the vitamins, however, originally thought to be single, have been shown to be mixtures of several vitamins, which have to be distinguished by numerals, *e.g.* vitamin B_1, vitamin B_2, etc.

Vitamin A.—This vitamin is of importance in promoting growth in children. It also improves the health of the skin and of the mucous membranes of the respiratory passages, and for this reason it gives increased resistance to bacterial infection. When this vitamin is absent from the diet for prolonged periods, night blindness, or inability to see in a dim light, and later, xerophthalmia, an infective inflammation of the eyes, supervene.

Chemical investigation has shown that the forerunner of vitamin A is a hydrocarbon, *carotene*, which has a large and complex molecule and a composition represented by the formula $C_{40}H_{56}$. This compound is found widely distributed in the vegetable kingdom: in tomatoes, apricots, bananas; in carrots, spinach, lettuce and grass, and in various marine algæ. Carotene, when taken into the animal organism, is decomposed by water (hydrolysed) with production of vitamin A, a compound which has been shown by chemists to have its molecule built up as indicated by the formula:



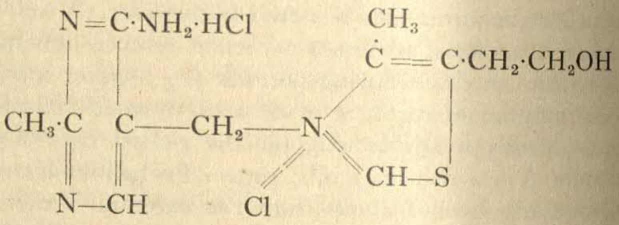
It is formed by the splitting of the carotene molecule into two parts and the combination of each part with two atoms of hydrogen and one atom of oxygen.

Man may obtain the necessary supply of vitamin A either from the carotene present in various vegetable foodstuffs or, ready formed, from foodstuffs, *e.g.* milk, butter, eggs, etc., derived from animals which have formed it from the carotene in their food. Any excess of the vitamin above that needed to satisfy immediate requirements is stored in the liver. A well-nourished person, therefore, possesses a certain reserve of vitamin A on which he can draw during periods (*e.g.* winter months) when fresh supplies of carotene or of ready-formed vitamin may not be so readily available. By far the richest natural sources of vitamin A are fish-liver oils, especially halibut-liver oil. This vitamin has been formed from the carotene present in green marine algæ and has been stored up in the liver of the fish. From these fish-liver oils the vitamin is now extracted and placed on the market in a standardized and highly concentrated form, so that it is now very easy to make good any deficiency of this vitamin in the diet. In Great Britain it is always added to margarine. Vitamin A is now not only extracted from fish-liver oils but is also produced synthetically on an industrial scale.

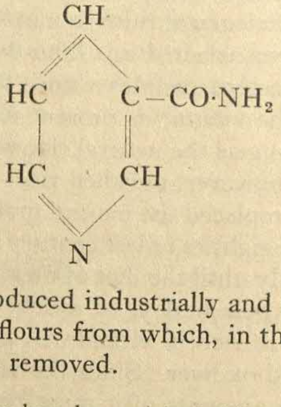
Vitamin A is necessary to regenerate visual purple, the light-sensitive substance in the retina, and it has been found that daily doses of carotene relieve eye-strain, reduce fatigue and increase the efficiency of workers engaged in matching colours.

Vitamin B_1.—Deficiency of this vitamin leads to the dangerous neuritic disease known as beri-beri. This disease was particularly prevalent among Eastern peoples whose food consisted mainly of fish and rice. The vitamin is present in the germ or embryo of the rice and so long as the natural rice was used, beri-beri did not occur. When, however, polished rice, from which the germ has been removed, replaced the natural grain, the disease became rampant, and in the eighties of last century sailors of the Japanese Navy suffered greatly until the diet of meat and polished rice was supplemented by whole barley, in which vitamin B_1 is present. Foodstuffs which are rich in vitamin B_1 are yeast, wheat germ, egg yolk, lentils and ox liver. Since the vitamin is not stored in the body, adequate amounts of it must be supplied in the daily diet.

The composition and molecular structure of vitamin B_1, the first crystalline vitamin to be obtained (in 1926) in the pure state, have been ascertained by chemists; and the compound, $C_{12}H_{17}ClN_4OS.HCl$, to which the name *thiamine*, formerly aneurine, has been given, is now produced synthetically on an industrial scale. How complex is this structure which chemists have succeeded in building up will be understood from the formula:



Vitamin B_2, which is present in yeast, meat, fish and milk, has been shown to be a complex of a number of different vitamins, of which, however, only two need be mentioned here. The more important of these is effective in preventing the disease called pellagra, from which thousands have died in the past and from which many still suffer. This vitamin has been found to be identical with *nicotinamide*, a compound which had been known to chemists long before its vitamin activity was recognized in the B_2 complex. It is the simplest of all the vitamins in its molecular structure which is represented by the formula:[1]



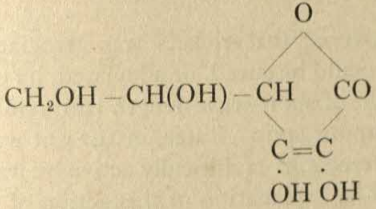
The compound is produced industrially and is added, especially in America, to white flours from which, in the milling of wheat, the vitamin has been removed.

---

[1] It will be noted that we have here a 'ring' of five carbon atoms and one nitrogen atom.

A second constituent of the B_2-complex is identical with the yellow pigment *riboflavin* and is present in milk, liver, egg-white, green vegetables, etc. Its composition is given by the formula $C_{17}H_{20}N_4O_6$. This substance is specially valuable as a preventive of cheilosis in man (which manifests itself in an inflammation on the lips), and of 'curled toe' in poultry. It is frequently added to poultry feeding stuffs to ensure good egg production. Riboflavin has been synthesized chemically, but is produced industrially by a micro-biological process.

Vitamin C.—This is the antiscorbutic vitamin; the vitamin which is effective in preventing scurvy. This vitamin, which was known to be present in fresh green vegetables and in citrus fruits,[1] was, in 1932, isolated in a pure crystalline state and in relatively large amount from Hungarian red pepper (paprika), and in the following year its constitution was ascertained and its synthesis effected. This compound, identical with vitamin C, is known as *ascorbic acid*, and has the constitution



Ascorbic acid (vitamin C) is now produced industrially from glucose or from an isomeric sugar, galactose, and is thus made readily available to all. It is optically active and rotates the plane of polarized light to the right. The lævo-rotatory acid can also be prepared, and this is found to have no anti-scorbutic effect. This is a further example of the difference in behaviour of two optically active isomers towards the molecularly asymmetric living tissues to which reference has already been made.

An adequate intake of vitamin C is necessary not only to prevent obvious signs of scurvy, but also to maintain satisfactory health. Deficiency of the vitamin may have as its effects, slow growth in children, slow healing of wounds and diminished resistance to infection.

Vitamin C, it may be noted, is rather sensitive to oxidation by the oxygen of the air, and much of the vitamin present in green vegetables, for example, may be destroyed by prolonged cooking.

---

[1] Zakatalsk nuts, grown in Russia, are said to have a vitamin C content about forty times that of lemons or oranges.

Vitamin D.—Rickets, which is generally associated with an imperfect calcification of the bones and teeth, is brought about not only through the absence of the necessary calcium salts and phosphates but also through absence or deficiency of vitamin D, a term now used to denote a group of different substances which have anti-rachitic properties. Even when the necessary salts are present, this vitamin is required for their proper utilization. Although the obvious signs of rickets—curvature of bones, knock knees, etc.—may be absent, radiological examination may reveal the presence of this disease in apparently healthy children. In adults, also, deficiency of vitamin D may be the cause of an imperfect utilization of calcium and phosphorus salts which may finally manifest itself in osteomalacia (a softening of the bones).

The most effective natural source of vitamin D is one of the fish-liver oils, *e.g.* cod-liver oil and, more especially, halibut-liver and tunny-liver oil.

In 1919 it was discovered that rickets was associated with absence of sunlight and could be cured, or alleviated, by exposure to sunlight or to the light of short wave-length (ultraviolet light) emitted by a mercury vapour lamp. Later, in 1924, it was found that foods could be rendered anti-rachitically active by irradiation with ultraviolet light. The explanation of this action of sunlight or of ultraviolet light, whether emitted by the sun or by a mercury vapour lamp, was obtained when, in 1927, it was found that a substance, *ergosterol*, which is present in plants (*e.g.* ergot), yeast, etc., is converted by the light into a compound which is anti-rachitically active. This compound was isolated in the crystalline state in 1932 and was called *calciferol*. It is now called *ergocalciferol* or vitamin D_2. It is enormously more potent than cod-liver oil, a tablespoonful of which contains only one-millionth of an ounce of the pure vitamin.

By the irradiation of cholesterol (dehydrocholesterol), which is present in the glands and skin of animals, *cholecalciferol* (denoted by D_3) is obtained. This differs structurally from ergocalciferol only very slightly. It is the form of the vitamin present in fish-liver oils.

In animals, the natural vitamin appears to be formed on the surface of the skin and is then absorbed by the body. This fact suggests that the anti-rachitic benefits of sun-bathing may be destroyed by subsequent bathing in water, unless sufficient time is given for the D_3 to be absorbed by the body.

Pure calciferol is now an article of commerce and can be used, when necessary, to supplement the natural supply of vitamin D in the daily diet. Addition of calciferol is now usually made to margarine.

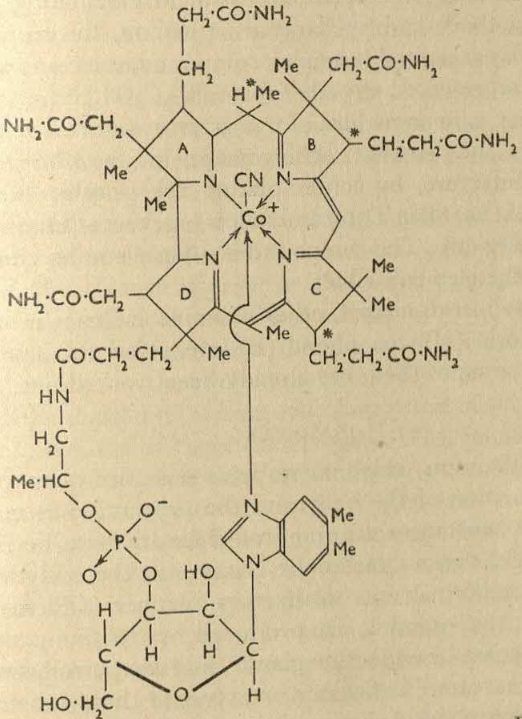


FIG. 28.—MOLECULAR CONSTITUTION OF B_{12}
(By permission Sir Alexander Todd)

Vitamin B_{12}.—This is one of the most notable of the vitamins and is remarkable for its curative action in cases of pernicious anæmia. It is present in liver and was obtained in the pure state in 1948. Later, the surprising discovery was made that the mould *Streptomyces griseus* is a much more abundant source of the vitamin for the commercial production of which it is now used. Sufferers from pernicious anæmia, which formerly could be controlled only by diets of raw liver, can now obtain by means of this vitamin, a substance known as *cyanocobalamin*, the same protection as is afforded to diabetics by insulin (p. 281).

Recently chemists have been successful in elucidating, both by chemical methods and by X-ray examination, the molecular structure of this exceedingly complex compound, the composition of which is represented by the formula $C_{63}H_{90}N_{14}O_{14}PCo$. The reader may gain some idea of the greatness of this achievement, perhaps the greatest achievement in the domain of molecular architecture, by contemplating the graphic formula devised by Sir ALEXANDER TODD and fellow-workers at Cambridge and shown in Fig. 28. The compound is unique among vitamins in containing the element cobalt.

Besides those just discussed, other vitamins are known—pyridoxin (B_6), biotin (H), tocopherol (E), etc.—and the synthetic production of some of them has already been worked out.

HORMONES

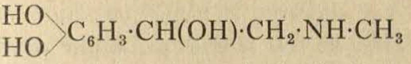
Besides the vitamins which, as we have seen, are essential for the proper nutrition of the body and the prevention of certain diseases, other substances are required if health is to be maintained and if the various metabolic changes in the body are to take place in a normal and satisfactory manner. These substances, unlike the vitamins, are produced by the living animal cells in the ductless or endocrine glands, and are passed directly into the blood stream. Deficiency or excess of these substances brings about physiological abnormalities or disease. The purpose of these glandular secretions is to excite or arouse certain responses or reactions and, for this reason, they are called hormones.[1] They are, however, not always stimulating or activating, they may also be restraining. They are, in general, regulators of the metabolic changes in the body.

The first of the hormones to be discovered was *adrenaline*, a secretion of the adrenal or suprarenal glands. It was first isolated in 1901 from the suprarenal glands of sheep and oxen, close on 1,000 lb. of tissue (the glands from 20,000 oxen) being required to yield 1 lb. of adrenaline.

---

[1] From the Greek *hormao*, to excite or to arouse.

After adrenaline had been obtained in the pure state it was not long before chemists had determined its composition and molecular structure and had shown them to be represented by the formula:



$$\begin{matrix}HO\\HO\end{matrix}\!\!>C_6H_3\cdot CH(OH)\cdot CH_2\cdot NH\cdot CH_3$$

Adrenaline is now produced synthetically from *catechol*, $C_6H_4(OH)_2$, a substance which is formed in the dry distillation of catechu or cutch, a hard gum secreted by certain species of *acacia* and other trees and used in tanning and in calico-printing. The synthetic adrenaline is placed on the market under the name *suprarenine*.

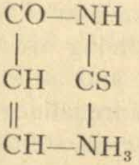
When injected subcutaneously, even in excessively minute amount, adrenaline (called in America *epinephrine*) causes a sudden, but transient, rise in the blood pressure, due to its constricting effect on the blood vessels.

Adrenaline, as formed in the glands of animals, is optically active and rotates the plane of polarized light to the left; whereas the synthetic product is a racemic compound of the two optically active forms, and is therefore inactive. With the help of dextro-tartaric acid, however, this racemic form can be resolved into its two optically active isomers, and the lævo-form isolated.

The difference in the behaviour of an optically active substance towards the asymmetric living tissues was emphazised in a previous chapter (p. 210), and an excellent illustration of this property is afforded by adrenaline; for it is found that the physiological action (the increase of the blood pressure) is twelve to fifteen times greater in the case of the naturally occurring lævo-adrenaline than in the case of the synthetic dextro-adrenaline and about twice as great as in the case of the inactive racemic form.

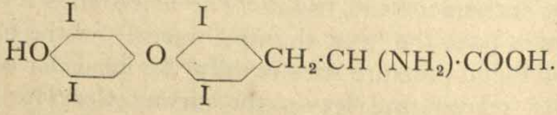
In the suprarenal glands, the adrenaline is probably stored as a readily decomposable compound with a protein, and during periods of emotional disturbance its production increases. When adrenaline is introduced into the blood, 'it produces all the vascular and visceral reactions which accompany the emotions of danger, excitement and fright. The hair stands on end, the face becomes pale, the heart thumps urgently on the chest wall, the arterial blood pressure rises rapidly, the muscular coat of the bronchioles relaxes and leaves the airway clear for vigorous breathing, and glucose, the fuel of the muscular machine, is poured from the carbohydrate depot of the liver into the blood stream.' The presence, however, of minute quantities of this hormone in the blood is necessary for the maintenance of a healthy tone.

Thyroxine.—This is the active principle of the hormone, thyroglobulin, formed in the thyroid gland. The hormone is needed in order to maintain the 'basal metabolic rate,' or the rate of heat production through oxidation in the body at rest, at its most advantageous value. If the thyroid secretion is absent or deficient in amount in infancy, cretinism, or a halt in the mental and physical development, occurs; and in adults there is a slowing down of the life processes, accumulation of fat, and a mental dullness and sluggishness, which are the symptoms of the disease known as myxœdema. These diseases can be cured or prevented by the administration of extract of the thyroid gland. If there is hypertrophy of the thyroid gland, leading to an excessive production of the hormone, the consumption of oxygen is unduly accelerated, the life processes take place too rapidly, and the restlessness and nervous debility characteristic of exophthalmic goitre (Graves' disease) supervene. This can be countered by administration of the compound *thiouracil*



or derivatives of it. Thiouracil brings about a slowing down of the metabolic processes and weight is put on. When it is added to the diet of cattle, sheep, pigs, etc., there is an increase of weight with less food.

In 1915 the active principle of the thyroid gland hormone was isolated in a crystalline form and called *thyroxine*; and in 1926 its constitution was determined and its synthesis effected. Thyroxine was thus shown to be a compound containing iodine and to have the formula,



This compound is now synthesized industrially at a cost lower than that of the substance extracted from the thyroid gland, and can be used in place of the extract in the treatment of cretinism and myxœdema. The naturally occurring thyroxine is lævo-rotatory, while the synthetic product, is, of course, inactive (racemic). This product, however, can be resolved into the two oppositely active isomers—dextro-rotatory and lævo-rotatory thyroxine. The lævo-rotatory form is three times more active physiologically than the artificially produced dextro-rotatory isomer, another example of the difference in action of two optically active isomers on natural tissues.

The characteristic feature of thyroxine is its content of iodine, and this element, in the form of iodides or other compounds of iodine, must be taken into the body to furnish the necessary iodine. Failure to satisfy this requirement leads to goitre, or an enlargement of the thyroid, due to an attempt to increase the production of thyroxine. Hence the use of iodides in the treatment of goitre. Long ago, burnt sponge was used, and the effectiveness of this remedy became intelligible when it was shown that sponges, seaweeds, etc., contain iodine in combination. Normally, iodine is taken in with the food or drinking water; and the main sources of this element are fish, crabs, lobsters, oysters, green peas and beans.

In Great Britain, 20–30 parts of potassium iodide per million are added to table and cooking salt to prevent goitre and thyroid enlargement.

Insulin.—Another hormone which is essential for the maintenance of health is insulin. This is produced in the pancreas and its main purpose seems to be to control the carbohydrate metabolism, or the changes which carbohydrates (sugars and starches) undergo in the body. A diminution in the production of insulin leads to a failure of the body tissues to burn and to store sugar (in the form of glycogen) in the liver. The content of sugar in the blood increases above the normal and brings about the state known as diabetes. Defective production of insulin by the pancreas can be made good by the subcutaneous injection of insulin, but excess must be avoided.

Insulin, which has been obtained in crystalline form, is a highly complex protein the composition of which is represented by the formidable formula, $C_{254}H_{377}O_{75}N_{65}S_6$. Its molecular constitution has also been unravelled and its synthetic production may one day be worked out. At present the active principle is extracted from the pancreas of the ox, pig or sheep, and this extract is used in the treatment of diabetes.

Besides the hormones just mentioned, there exist also a number which are associated with and are indispensable for normal and healthy sex activity, and the appearance of the secondary sex characteristics. Chemists have been very successful in elucidating the nature of the sex hormones, which are related chemically to the compounds cholesterol and ergosterol already mentioned. Not only have some of these hormones been synthesized, but chemists have also prepared substitutes, which are now produced industrially. These synthetic compounds can be successfully used clinically in place of the natural hormones to which, indeed, for many purposes, they are to be preferred.

Great hope was at one time inspired that a cure for rheumatoid arthritis had been found in *cortisone*, a hormone produced in the cortex of the suprarenal glands of oxen, and now produced industrially from Mexican yams and from the juice of sisal leaves. Although this hope has been disappointed, cortisone is not without its therapeutic value in the treatment of certain diseases.

The adrenocorticotrophic hormone, ACTH, produced in and extracted commercially from the pituitary glands of pigs (especially) and oxen, is found to be valuable therapeutically for the treatment of acute rheumatoid arthritis, and is also used in the treatment of asthma, leukæmia, hæmolytic anæmia, etc.

From the discussion of the phenomena of catalysis (*Chap.* 7) one could not fail to realize the importance of minute quantities of certain substances in influencing the rate of chemical change; and in the vitamins and hormones we meet with substances which seem to exercise some sort of catalytic effect in regulating the various chemical processes which go on in the living plant or animal organism. The presence of these substances, even though their amount may be extremely small, is of vital importance for health. The study of how even minute amounts of certain substances may completely change the state of health of man or of the animals is clearly one which exercises a peculiar fascination; and just as it became known, through the investigations of chemists, that certain small amounts of iodine (in a combined state) must be present in the food in order that the secretion of the thyroid gland may be effective, so it has been found that traces of a number of other elements (*trace elements*) are essential for the health of man or of the animals. Reference has already been made to the importance of trace elements for the health of plants.

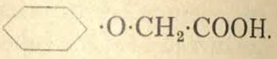
That iron, which is a constituent of hæmoglobin, is essential for health has long been known, but it is only in recent years that it has become known that the presence of minute quantities of copper is necessary for the efficient transference of the iron into hæmoglobin, and many cases of pernicious anæmia are due to a deficiency of copper. The daily intake of copper for an adult should be about 4–5 milligrams, and if this is not supplied in the food, health is impaired. In many cases, severe wastage diseases among animals have been cured by the addition of small quantities of copper salts to the diet.

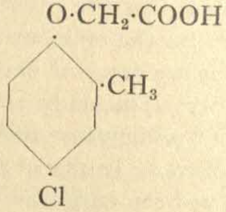
Small quantities of manganese salts are necessary for the proper development of the fœtus, and deficiency of cobalt has been found to be the cause of 'bush sickness' or 'pine' in sheep and cattle (Plate 35). It may be cured by adding cobalt salts to the soil (whence it passes into the pasture) or to the salt licks. As little as 1 milligram of cobalt per day is sufficient to secure health. It may be noted, also, that trace elements, especially zinc and manganese, are intimately connected with the proper utilization of vitamins by the body and are generally associated with the natural vitamins. They are, of course, not present in the synthetic vitamins.

PLANT GROWTH-REGULATORS

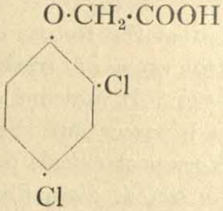
Stimulated by the discovery that in plants, as in animals, hormones are produced which control the growth and general health of the plant, chemists sought to prepare synthetically not only the naturally occurring compounds but also others which might have a similar or even a greater growth-regulating action. In this they have been very successful, and many compounds have now been prepared, and produced industrially, which, as has already been mentioned (p. 136), render great service in agriculture and horticulture.

Of the many growth-regulating compounds which have found practical application only a few of the more important can be mentioned here.

1. *Selective weedkillers.*—The two compounds found to be most useful as selective weedkillers (p. 136) are derivatives of an acid known as phenoxy-acetic acid,  This acid, in itself, is not effective, but two derivatives are extensively and successfully used. These are 2-methyl-4-chlorophenoxyacetic acid,

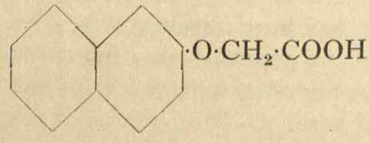


and 2:4-dichlorophenoxyacetic acid,



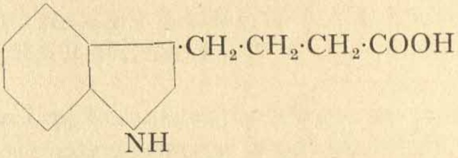
in which the hydrogen atoms in the 2 and 4 positions in the benzene ring (p. 202) are replaced by CH_3– or Cl–. The former compound, named *methoxone*, is generally referred to as MCPA; and the latter as 2:4–D.

2. *Parthenocarpy.*—Although the stimulus for the production of fruit usually comes from pollination or fertilization in the flower, it has been found that the production of fruit may, in a number of cases at least, be stimulated by hormones, natural or synthetic. This production of (seedless) fruit by unfertilized flowers is known as *parthenocarpy*. In the tomato, especially, the production of parthenocarpic fruit can be readily stimulated by spraying the flowers with various plant growth-regulators, such as β-naphthoxyacetic acid (NoXA),

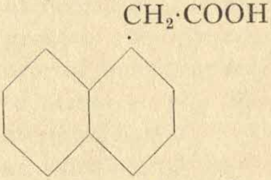


By this means the yield of fruit may be very greatly increased (Plate 36).

3. *Rooting of cuttings.*—The formation of roots by plant cuttings is stimulated by a number of substances, such as β-indolebutyric acid (IBA),

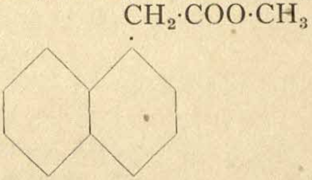


and α-naphthylacetic acid (NAA),

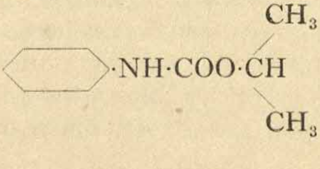


4. *Inhibition of potato sprouting.*—Normally the buds (eyes) of a potato remain dormant for a certain period, owing to the presence of a growth-inhibitor in the skin. This period of dormancy, however, can be broken by treatment of the potatoes with a substance known to chemists as ethylene chlorhydrin; and by this means new potatoes may, under suitable climatic conditions, be used as 'seed' for a second crop.

When, however, potatoes are stored for food, it is desirable to prolong the period of dormancy and to prevent sprouting. This also chemists have been successful in achieving by means of the synthetic compound methyl-α-naphthylacetate (MeNA),



and still more effectively by means of the compound isopropylphenylcarbamate,



To fruit growers, chemists have rendered a further service by supplying them with substances, *e.g.* 2:4–D, MCPA, NAA, which, when sprayed on apple and pear blossom, prevent the premature dropping of the fruit.

Chapter 17

FROM THE CROOKES TUBE TO THE NUCLEAR REACTOR

ALTHOUGH the atomic theory, formulated by Dalton in 1803, was generally accepted as a guiding principle in physical science, it was regarded by some merely as a convenient 'working hypothesis,' useful but not necessarily representing actual fact. No direct, experimental proof of the objective reality of atoms existed. Investigations, however, belonging mainly to the present century, have contributed, from several different directions, towards establishing the atomic theory in a position of unassailable strength, and have furnished a proof of the objective reality of atoms or discrete particles as constituting the fundamental basis of matter. By the phenomena of diffusion, more especially diffusion of gases; by the Brownian movement observed in the case of minute particles in suspension (*Chap.* 11); by the phenomena of radioactivity (p. 290), and even by the blue colour of the sky (p. 184), the discontinuous structure of matter is made manifest and the existence of atoms or discrete particles established with a probability amounting to a certainty.

To Dalton, as to Newton, the atoms were 'solid, massy, hard, impenetrable particles,' incapable of subdivision; but during the greater part of the nineteenth century the ground was being prepared for a revision of this view. To this work of preparation attention must now be given.

As the determinations of atomic weights increased in number, it was observed that most of the values, when referred to the atomic weight of hydrogen as unity, were either whole numbers or very nearly whole numbers. This remarkable fact gave rise to the view, first put forward in 1816 by WILLIAM PROUT, a physician and Lecturer on Chemistry in London, that the atoms of different substances are made up of various amounts of some primordial matter, and that this primordial matter is hydrogen. This view, however, did not meet with general acceptance, because it was found that the deviation of the atomic weights of a number of the elements from whole multiples of the atomic weight of hydrogen could not be explained as due to experimental error. Many chemists believed, however, that although they could not accept Prout's view, it contained some element of truth; and this belief was strengthened when, in 1901, the Hon. R. J. STRUTT (later, 4th Baron Rayleigh), by applying the law of probabilities, showed that 'the atomic weights tend to approximate to whole numbers far more closely than can reasonably be accounted for by any accidental coincidence.' How nearly the hypothesis of Prout agrees with present-day views regarding the constitution of the atom will become clear in the sequel.

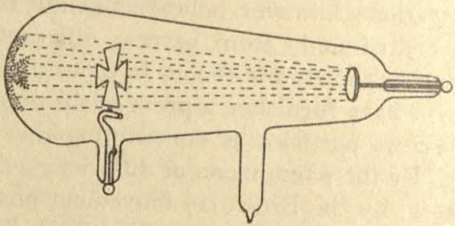


FIG. 29.—CROOKES TUBE

Cathode Rays.—The new light which, during the present century, has been shed on the problem of the constitution of matter came first from an unexpected direction, namely, from a study of the discharge of electricity through highly rarefied gases. In 1859, it was discovered by the German physicist PLÜCKER, that when an electric discharge is allowed to take place in a highly evacuated glass tube, a peculiar radiation is projected from the negative electrode or *cathode*, as it is called; and this radiation excites a fluorescent light in the glass of the tube opposite the cathode. This radiation, moreover, known as the *cathode rays*, travels in straight lines, and if a solid object is placed in the path of the rays, a shadow is cast (Fig. 29). Moreover, by using a concave cathode, whereby the rays can be brought to a focus, iridioplatinum can be melted, under the fury of the bombardment by the cathode rays. These phenomena were studied more especially by Sir WILLIAM CROOKES who, in 1879, surmised that the cathode rays, which he called 'Radiant Matter,' were composed of extremely small particles; and he concluded a lecture, delivered before the British Association, with the words: 'We have actually touched the borderland where Matter and Force seem to merge into one another. . . . I venture to think that the greatest scientific problems of the future will find their solution in this Border Land . . . here, it seems to me, lie Ultimate Realities, subtle, far-reaching, wonderful.'

The experiments of Crookes aroused a very great and widespread interest, fascinating the layman by the spectacular beauty of the unfamiliar phenomena and stimulating men of science to a further investigation of these phenomena and of the nature of the 'Radiant Matter,' or cathode rays. It is, in fact, to Crookes' enthusiasm and to his recognition of and insight into the underlying significance of the phenomena accompanying the discharge of electricity through rarefied gases that we owe the investigations of J. J. Thomson, Röntgen, Becquerel, Rutherford and the rest, which led, by a sort of evolutionary process, to the discovery of X-rays, radioactivity and, at last, to the nuclear reactor and the successful utilization of nuclear energy.

The experimental investigation of the nature of the cathode rays was undertaken by Sir JOSEPH J. THOMSON, Cavendish Professor of Physics in the University of Cambridge, who, in 1897, proved that they consist of negatively charged particles which travel with the enormous velocity of from 10,000 to 100,000 miles per second, the latter velocity being such that the particles would engirdle the earth four times in the space of a second.

Thomson showed, moreover, that the mass of these negatively charged particles or *electrons*, as they are called, is exceedingly small and equal only to one eighteen-hundred-and-fortieth ($\frac{1}{1840}$) of the mass of the hydrogen atom, the lightest atom or lightest particle of matter hitherto known.[1] In this way, the existence of particles very much lighter than the chemical atom was discovered; and since it was found that electrons are given off by different substances under various conditions, as, for example, when a body is raised to incandescence,[2] the conception of the electronic constitution of matter, *i.e.* of the atom, arose.

---

[1] The mass of a hydrogen atom has been calculated to be $1{\cdot}67 \times 10^{-24}$ gram (*i.e.* 1·67 divided twenty-four times by 10), and the mass of an electron is therefore $9{\cdot}11 \times 10^{-28}$ gram. In other words, it would take about one million million million million atoms of hydrogen to make up the weight of 1 gram (15·4 grains).

[2] As in the 'valve' used in wireless telephony.

From another direction, also, further impressive evidence was soon obtained that the atom is no longer to be thought of as a single, indivisible, unchangeable particle, but as a vibrant microcosm, a complex system possessing enormous potential energy and capable, in certain cases at least, of undergoing an amazing and spontaneous transformation into atoms of a different kind.

Radioactivity.—In 1895, the German physicist, KONRAD VON RÖNTGEN, while studying the electric discharge in a Crookes tube, made the sensational discovery of X-rays. In the following year, the French physicist, HENRI BECQUEREL, thinking that X-rays might have their origin in the fluorescence produced by cathode rays in the glass of the tube, investigated the effect on a photographic plate of a salt of uranium which fluoresces under the action of light. He was thereby led to the discovery that uranium continuously and spontaneously emits 'rays' or radiations which pass through wood, paper and other opaque materials, and affect a photographic plate in a manner similar to X-rays. In this way, Becquerel discovered the property of *radioactivity*. These radiations or 'rays' also have, like X-rays, the power of rendering the air electrically conducting; and this fact is made use of for their detection through the discharge of a gold-leaf electroscope, or by means of another electrical apparatus, the Geiger-Müller counter.

Further investigation of radioactive phenomena by Professor PIERRE CURIE and his wife, MARIE SKLODOVSKA CURIE, in Paris, led to the discovery, in 1898, of the much more highly radioactive element radium, which occurs, to the extent of about one part in 10,000,000, in the uranium-containing mineral, pitchblende. From this mineral, by a long and laborious process, Mme Curie later prepared the salt of radium, radium chloride, a white substance similar in appearance to common salt. Although the element radium has been isolated, and has been found to resemble, in its chemical properties, the metals calcium and barium, it is in the form of its chloride that it is generally employed; and when, in ordinary language, one speaks of radium, it is to this salt, radium chloride, that one generally refers.

Radium was originally obtained from deposits of pitchblende (uranium oxide) occurring at Joachimstal in Czechoslovakia, but, since 1930, almost the whole of the world's supply of this element has been obtained from the Katanga Mines in the Belgian Congo and from the deposits of pitchblende which are found on the shores of the Great Bear Lake in northern Canada.

Radium is a substance which must be handled with care, for, if kept for a short time near the body, it cauterizes the skin and produces a sore which is difficult to heal. It is used extensively in the treatment of cancer and other malignant growths.

The investigation of the radioactive elements uranium, thorium, actinium and radium showed that three different kinds of rays or radiations are emitted, known as alpha, beta and gamma rays. The alpha rays are positively charged particles of atomic dimensions (p. 293), and are easily stopped by a sheet of paper or even by a few centimetres[1] of air. These alpha particles, however, which are shot out with a speed of some ten thousand miles a second, have great energy and are more effective than the beta or gamma rays in breaking up the atoms of the atmospheric gases, whereby the air is rendered a conductor for electricity. They are, of course, all stopped by the walls of the glass or metal tube in which, ordinarily, the small quantities of radium salt are sealed up.

The beta rays are negatively charged electrons; and the gamma rays are electromagnetic vibrations of very short wavelength, similar in nature to X-rays. The beta and, more especially, the gamma rays are highly penetrating.[2]

Electrical measurements have shown that the naturally occurring radioactive elements uranium, radium, thorium and actinium give rise, through the loss of an alpha or beta particle, or through the emission of gamma rays, to different series of radioactive elements which have a more transient existence. Thus, atoms of radium emit an alpha particle and become atoms of a gaseous element *radon*, from which, by the loss successively of an alpha or beta particle, there is formed a whole series of radioactive elements, radium A to radium G, now recognized as *isotopes* (p. 297) of bismuth, lead, etc. Radium G is not radioactive and is chemically identical with lead.

---

[1] A centimetre (cm.) is rather less than half an inch; 2·54 cm. = 1 inch.

[2] It is these very penetrating rays that destroy the unhealthily growing cells in cancer.

TUTE OF EDUCATION FOR
Dept. of Extension
SERVICE.

Although the fact of radioactivity is now familiar to all, the phenomena of radioactivity were, in the closing years of the nineteenth century, startling in their unexpectedness; and they were bewildering and inexplicable until, in 1902, ERNEST RUTHERFORD (afterwards Lord RUTHERFORD) and FREDERICK SODDY put forward their now universally accepted hypothesis of *atomic disintegratiom.* According to this hypothesis, the atom of a radioactive element is a complex system of particles which undergoes spontaneous change, or explodes, as it were, with projection at a very high velocity of negatively charged electrons (the so-called beta rays), or of heavier, positively charged particles, the alpha rays. Not all the atoms, however, of a radioactive substance undergo disintegration at one moment; only a certain definite fraction of the atoms reaches the condition of instability at the same time, and the fraction is different for each radioactive element. In the case of radium, for example, only about one atom out of every hundred thousand million breaks up each second. According to the Rutherford-Soddy theory, the different radioactive elements can be distinguished from one another by the rate at which atomic disintegration takes place, or the rate at which the radioactivity diminishes or 'decays.' This is generally expressed in terms of the time required for the radioactivity to be reduced to one-half or for half the atoms to undergo disintegration. This is called the 'half-life' of the element. The half-life of uranium is rather less than five thousand million years, and that of radium 1,590 years. This means that half the radium now existing will have disappeared at the end of 1,590 years, and half of what then remains will have disappeared at the end of a further period of 1,590 years, and so on. Fresh amounts of radium, however, are constantly being formed, at a slow rate, by the disintegration of the parent element uranium. This accounts for the presence of radium in all uranium minerals.

Radon, which is constantly being formed by the disintegration of radium atoms, has a short half-life of 3·825 days. It is, therefore, highly radioactive and is employed in radiotherapy in place of or in addition to radium.

One of the disintegration products of thorium, known as mesothorium-1, is obtained in considerable quantities as a by-product of the incandescent gas-mantle industry. Mesothorium-1 loses half its radioactivity in 5½ years, so that its life is comparatively short; but for that very reason highly active preparations can be obtained. The commercial mesothorium is largely employed in the manufacture of luminous paints (*e.g.* zinc sulphide excited to luminescence by the alpha particles emitted by mesothorium), which can be applied, for example, to the hands of watches and so make it possible for the time to be read in the dark.

A striking confirmation of the correctness of the disintegration hypothesis of radioactivity and of the complexity of atoms was obtained when Sir WILLIAM RAMSAY and Lord RUTHERFORD showed, by direct experiment and in different ways, that the positively charged alpha particle which is expelled from radioactive substances is in fact a positively charged helium atom, or a helium atom which has lost two electrons. Not only did Rutherford isolate the alpha particles and show that on losing their electrical charge by taking up electrons they form ordinary helium, he also succeeded in counting the number of alpha particles emitted by a given weight of radium, by allowing the particles to pass through a small hole and impinge on a fluorescent screen. At each impact of an alpha particle, a little flash of light was produced, and by counting the number of flashes the number of particles passing through the opening was obtained. Since the number of alpha particles expelled from a given weight of radium can be counted, and since each alpha particle becomes a helium atom, it is possible, by measuring the volume of helium produced by a given weight of radium in a given time, to calculate the number of helium atoms (or molecules) in a given volume of the gas. The number obtained by Lord Rutherford, namely, twenty-seven trillion five hundred thousand billion ($2{\cdot}75 \times 10^{19}$), in 1 cubic centimetre at 0° C. (32° F.), is in good agreement with the value deduced from measurements of an entirely different kind.[1]

According, moreover, to a well-known law of Avogadro, *equal volumes of all gases when under the same pressure and at the same temperature, contain the same number of molecules.* It follows, therefore, that at 0° C. and under standard atmospheric pressure (76 cm. of mercury), 1 cubic centimetre of any and every gas will contain $2{\cdot}69 \times 10^{19}$ molecules, to use a more accurate number than that obtained by Lord Rutherford.

---

[1] In the above statement, a billion is taken as a million million, and a trillion as a million billion.

Atomic Structure.—The striking proof of the complexity of the chemical atom which was afforded by electrical and radioactive phenomena gave a great impetus to the formation of definite views regarding the inner structure or constitution of what was formerly thought of as indivisible. Since negatively charged electrons constitute part of the atom (p. 289), and since the atom as a whole is electrically neutral, it follows that there must be an amount of positive electricity within the atom equal to the total negative charge carried by the electrons. How, then, is the structure of the atom to be conceived?

Experiment showed that when alpha rays, from radium for example, were passed through a gas, most of the tracks were straight lines; some showed a slight bending, while a very few showed a sharp deflection. A similar behaviour was also found when alpha rays were passed through thin metal foil, *e.g.* gold leaf. In this case, some of the alpha rays were thrown back almost on their own tracks. From a study of these results, Lord Rutherford suggested that the positive electricity in the atom is concentrated in a very minute *nucleus*, in which, also, almost the whole mass of the atom is supposed to be resident. Around this minute positively charged nucleus revolve the negative electrons, like a sun ringed round with planets. This atomic model, elaborated somewhat by the Danish physicist, Niels Bohr, and confirmed by all later work, was a brilliant inference from experimentally determined data.

And what is the nature of the positively charged nucleus? The atoms or nuclei of some radioactive elements emit, on disintegrating, alpha particles or positively charged helium nuclei, while the nuclei of other radioactive elements emit beta rays or negatively charged electrons. In the case of the atoms of certain radioactive elements, therefore, we seem to have a proof that the positively charged nucleus of the helium atom is one of the units of nuclear structure; but since the mass of the helium atom (or nucleus) is nearly four times that of the hydrogen atom, the helium nucleus must itself be regarded as complex. The conclusion, therefore, is reached that the positively charged nucleus of the hydrogen atom, the lightest atom, is the simplest, positively charged unit of atomic structure. This unit is called a *proton.*

In the nucleus of atoms other than of hydrogen, the investigations of physicists have revealed the presence not only of positively charged protons but also of uncharged particles or *neutrons* (p. 301) produced, it may be, by the firm union of a proton and an electron. The mass of a neutron is sensibly equal to that of a proton.

The proton was for long regarded as being the unit of positive electricity, but in 1933 it was found that there is produced, under certain conditions, a particle which has the same mass as the electron, but which has a positive instead of a negative charge. This particle, therefore, to which the name *positron* has been given, must be regarded as the unit of positive electricity, just as the electron is the unit of negative electricity. A proton may pass into a neutron through the loss of a positron.

Modern investigations of the structure of the atom have extended enormously the limit of subdivision of matter; and the atom now takes the form of a very open-spaced system of particles, the diameters of which are very small compared with that of the system as a whole, or of the atomic domain as it has been called. The hydrogen atom, according to the modern view, consists of a positively charged nucleus, a minute speck of positively charged matter (the proton), round which, at a relatively very great distance, there circles a negatively charged electron. The structure of an atom of hydrogen, therefore, has been compared with that of the solar system, and it has been pointed out that since the diameter of the earth is one twenty-thousandth of the diameter of its orbit round the sun, one can think of a hydrogen atom as a system in which the earth represents an electron circling round a nucleus (much smaller than itself), at a distance equal to twice the distance of the earth from the sun. The atom, therefore, is mainly void, a thing of specks and spaces, mainly spaces; and one can readily understand how a positively charged alpha particle can pursue a straight path *through* the atoms of matter and be only occasionally deflected by a near approach to, or collision with, the relatively massive, positively charged nucleus (p. 294).

The atom of helium, the element of next higher atomic weight to hydrogen, has a mass four times that of the hydrogen atom, and its nucleus, which carries two positive charges, is to be regarded as being made up of two neutrons and two protons. Around this nucleus there circle two electrons. The atoms of the elements of higher atomic weight, similarly, are to be regarded as constituted of positively charged nuclei, built up of protons and neutrons, encircled by rings of planetary electrons; and the important discovery was made that *as one passes from element to element, the number of positive charges on the nucleus and, therefore, the number of planetary electrons surrounding the nucleus, increases by single units.*

Atomic Number.—The number of positive charges on the nucleus, or the number of protons in the nucleus, which determines the number of planetary electrons, is of much importance, because it is on these planetary electrons that the chief chemical and physical properties of the elements depend. One of the great advances made in modern times has been the recognition of the fact that the number of protons in the nucleus is the same as the serial number of the element in the periodic classification given on p. 17. This is called the *atomic number* of the element, and for its determination several methods are available. In the case, therefore, of uranium, the element of highest atomic weight occurring in nature, the atomic number of which is 92, the atom consists, it is believed, of a complex nucleus carrying a positive charge of 92 units, or containing 92 protons, surrounded by rings or shells of 92 electrons.

The recognition of the fact that the properties of an element depend on the atomic number, rather than on the atomic weight of the element, enables one to take account of the anomalies occurring in the Mendeléeff classification (p. 17), namely, that argon must, on account of its chemical properties, be placed before potassium, and similarly tellurium before iodine, although the atomic weights are in the reverse order. When the elements are arranged in the order of their atomic numbers, instead of their atomic weights, these anomalies disappear, and argon and tellurium fall into their proper places (p. 17). Generally, it is true, the atomic numbers and atomic weights follow the same order, but not always; and for the periodic recurrence of chemical properties it is the atomic number which is of importance. The periodic law, therefore, must now be stated in the form: *The properties of the elements vary in a periodic manner with the* ATOMIC NUMBER.

The existence of a series of integral atomic numbers throws important light on the possible number of the elements. On arranging the elements serially in the order of their atomic numbers, as in the table on p. 7, it is seen that between hydrogen and uranium, the elements of lowest and highest atomic numbers found occurring in nature, the series is complete; no gaps for undiscovered elements exist. The existence in nature, however, of two of the elements has still to be discovered. Beyond uranium a number of elements have been produced artificially and it may well be that still other elements of higher atomic number will someday be similarly obtained.

Isotopes.—From the modern theory of atomic constitution one can draw the important conclusion, in sharp contradiction of the main postulate of Dalton's atomic theory, that the atoms of an element need not all be alike. If, to the nucleus of a given atom, one or more neutrons be added, the mass of the atom will be correspondingly increased, but the number of protons, and therefore the atomic number, will be unaltered. The *chemical* properties, therefore, will also be unaltered.

By an electrical method, known as *positive ray analysis*, Sir J. J. THOMSON and Sir F. W. ASTON were able, as early as 1913, to determine the relative masses of the nuclei, and therefore of the atoms, of different elements; and they found that if the atomic weight of oxygen is represented by 16·0, the atomic weights of all other atoms are whole numbers.[1] Thus, for example, it was found that chlorine, as ordinarily prepared from sodium chloride and the atomic weight of which, determined chemically, is 35·46, consists of a mixture of atoms with atomic weights 35 and 37 respectively, mixed together in the proportion of about 3:1. The two varieties of atoms are *chemically* indistinguishable and are called *isotopes*, because, having the same atomic number, they fall into the same place in the periodic classification. The atomic number of chlorine is 17 and the nucleus of one isotope consists of 18 neutrons and 17 protons, while the nucleus of the other isotope consists of 20 neutrons and 17 protons. These isotopes are to be regarded chemically as varieties of the same element, chlorine; and are represented by the symbols Cl^{35} and Cl^{37}, where the numerals denote the atomic weight or, more correctly, the *mass number* of the isotopes, the mass number being the sum of the numbers of protons and neutrons in the nucleus.

---

[1] Slight divergences may be found, the explanation of which, however, cannot be discussed here.

All the elements can exist in isotopic forms, the separation of which is generally very difficult.

In view of the existence of isotopes one may now re-define an element as a substance all the atoms of which have the same atomic number, or have the same number of protons in their nuclei.

The existence of isotopes was first realized in the case of radioactive elements, but many isotopes of other elements, some stable and some radioactive, are now produced artificially.

In 1932 the very interesting discovery was made by Professor H. C. Urey and his fellow-workers in America that hydrogen, as ordinarily prepared, is a mixture of two isotopes, the lighter having the atomic weight 1 and the heavier the atomic weight 2, the nucleus, in this case, consisting of one neutron and one proton. For the lighter isotope the name hydrogen has been retained, and the heavier isotope was christened *deuterium* (symbol D). Whereas the isotopes of the elements of higher atomic weight differ only slightly from one another in their properties, deuterium differs quite markedly from hydrogen, as, indeed, one might expect from the fact that its atomic weight is twice that of hydrogen. 'Heavy water' or deuterium oxide, D_2O, the analogue of the hydrogen compound H_2O, freezes at 3·8° C. (38·8° F.) and has a density (1·11) which is 11 per cent. greater than that of hydrogen oxide. Deuterium oxide is present in ordinary water to the extent of about 1 part in 6,500 and can best be obtained by the prolonged electrolysis of water. Heavy water is now of much importance as a 'moderator' in a nuclear reactor (p. 308).

Another isotope of hydrogen, *tritium* (symbol T), the nucleus of which consists of one proton and two neutrons, has been produced artificially (p. 308). It is radioactive and undergoes spontaneous transformation into an isotope of helium (He^3), with the atomic weight 3, through the conversion of one neutron into a proton and the emission of an electron. It has a half-life of 12·4 years.

Planetary Electrons.—As one passes from element to element, the number of planetary electrons increases, at each step, by unity; and as their number increases, they group themselves in a number of shells or orbits around the nucleus. Hydrogen, with the atomic number 1, has only one planetary electron; helium has two planetary electrons, both in the same shell, and this system is a very stable one. Except in the case of helium, the maximum degree of stability is reached when the number of electrons in the outermost shell is eight, forming what is known as an *octet.*

On passing from helium to lithium and the other elements of the first short period (p. 17), a new shell of electrons, farther removed from the nucleus, begins to be formed; and this shell is built up by the successive addition of one electron until, with neon, the shell contains eight electrons. The octet is now complete, and the system is one of maximum stability.

Similarly, on passing from neon to sodium, a third shell of electrons begins to be built up, and so on.

It may be noted that although the number of electrons in the outermost shell never exceeds eight, the number in the inner shells may rise to thirty-two. Thus, in the case of radon, which belongs to the helium family, and has the atomic number 86, the numbers of electrons in successive shells, from the nucleus outwards, are 2, 8, 18, 32, 18, 8.

According to present views, it is the electrons in the outermost shell which are involved in chemical combination and which determine the chemical character, especially the valency of the element. The electronic systems of the atoms of the rare gases, in which the outermost shell consists of two (helium) or of eight electrons, are the most stable systems, and these elements are chemically inactive, or have zero valency. In other elements, valency may be regarded as an expression of the tendency of an atom to acquire the most stable electronic arrangement, namely that of the nearest rare gas.

The sodium atom, for example, has one electron in the outermost shell, and it readily gives up this electron so as to form a system having the arrangement of the nearest inert gas, neon. Chlorine, on the other hand, which has an outermost shell of seven electrons, readily takes up one electron to complete the octet, thereby forming a system which has the arrangement of the inert gas argon. Combination between sodium and chlorine, therefore, readily occurs by the transfer of one electron from the sodium atom to the chlorine atom; and since the sodium atom thereby becomes positively charged (sodium ion), and the chlorine atom negatively charged (chloride ion), the two atoms (or ions) are held together by electrostatic attraction. Sodium and chlorine are said to be univalent elements. Similarly, calcium can give up and oxygen can take up two electrons, and are therefore said to be bivalent. Valency thus appears as a measure of the number of planetary electrons which an atom has in its outermost shell in excess of or in defect of eight. This is known as *electro-valency*.

In many cases, however, combination between atoms depends not on the giving and receiving of electrons, but on the sharing of one or more pairs of electrons, so that each atom has eight electrons (or in the case of hydrogen, two electrons) in its outermost shell. Thus, in the combination of hydrogen with chlorine or with oxygen there is a sharing of electrons: $\mathrm{H}\overset{\times}{\cdot}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$ and $\mathrm{H}\overset{\times}{\cdot}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\overset{\times}{\cdot}\mathrm{H}$. The electron belonging to the hydrogen atom is represented here by a cross. This form of combination is an expression of what is called *co-valency*.

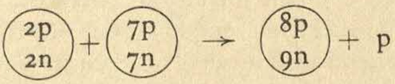
From the preceding discussion it will be evident how very nearly the hypothesis of Prout agrees with the now generally accepted views regarding the constitution of the atoms of different elements. Although the atoms of the elements are not to be regarded as built up of hydrogen atoms but rather of hydrogen nuclei (protons) and neutrons, together with planetary electrons, the idea underlying the two views is essentially the same; and as a result of recent investigations and deductions one is beginning to see more clearly something of the order and unity which run through the whole series of diverse elements known to the chemist.

By the investigations of the twentieth century the atomic or discontinuous constitution of matter has been established beyond any reasonable doubt; and in the process our views regarding the ultimate units of matter have undergone a change. To quote the words of the eminent French physicist, JEAN PERRIN: 'Atoms are no longer eternal, indivisible entities, setting a limit to the possible by their irreducible simplicity; inconceivably minute though they be, we are beginning to see in them a vast host of new worlds. . . . Nature reveals the same wide grandeur in the atom and the nebula, and each new aid to knowledge shows her vaster and more diverse, more fruitful and more unexpected, and, above all, unfathomably immense.'

Transmutation of Elements.—The knowledge which has been gained regarding the constitution of matter, and more especially the discovery of the phenomena of radioactivity, place in a new light the question of the transmutation of the elements, the achievement of which was one of the great aims of the mediæval alchemists.

The elements, such as we know them at the present day, consist, for the most part, of stable atomic systems. In the radioactive elements, however, we have atomic systems which pass spontaneously into a condition of instability and undergo a process of disintegration into simpler atomic structures. In this way, a transmutation, not of lead to gold but of radium or of thorium to lead, may be said to take place. This process of transmutation, however, is quite uncontrollable by man.

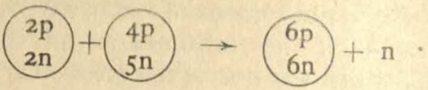
It was in 1919 that the first artificial transmutation of one element into another, by the disintegration of atomic nuclei, was effected by Lord RUTHERFORD. Atoms, as we have seen, are very open-spaced structures, and when atoms of nitrogen were bombarded by alpha particles (helium nuclei), liberated, for example, by the radioactive disintegration of radium, most of the particles passed in a straight line through the open structure of the atom. Some, however, of the particles, which are projectiles of great kinetic energy, registered direct 'hits' on the nucleus, and, in fact, penetrated into the nucleus of the nitrogen atoms. An unstable structure was thereby produced which immediately broke up with the emission of a proton and the production of a stable oxygen isotope of atomic weight 17. Thus, representing protons by p and neutrons by n, we can write:



$$He^4 + N^{14} \rightarrow O^{17} + p$$

Many other transmutations of a similar character were effected by various workers during the two decades following 1919.

In 1932 the important discovery was made by Sir JAMES CHADWICK, working in Rutherford's laboratory, that when the element beryllium is bombarded with alpha particles, carbon is formed with the emission, not of protons but of swift, penetrating, uncharged particles, or *neutrons*, the individual mass of which is sensibly equal to that of a proton. The transmutation can be represented thus:



$$He^4 + Be^9 \rightarrow C^{12} + n$$

These neutrons, now produced in large numbers in the nuclear reactor (p. 308), are very effective agents for the disintegration or transmutation of atomic nuclei, for, owing to the absence of an electric charge, they are not repelled by the nucleus of an atom and so can more readily enter into it. The unstable structure produced then breaks up into an atom of a different kind. Thus, when a neutron enters the nucleus of a sulphur atom, S^{32} (consisting of 16 neutrons and 16 protons), an unstable system is produced which passes into a radioactive isotope of phosphorus, P^{32} (consisting of 17 neutrons and 15 protons), and a proton is emitted. Such transmutations may actually be taking place in many naturally occurring minerals.

Rapidly moving protons and deuterons (positively charged nuclei of deuterium), their motions greatly accelerated by a powerful electric field, as in the apparatus known as a cyclotron, have also been used for the purpose of bringing about artificial transmutations, some of which have proved to be of much value. By the bombardment of atoms of the elements with these different missiles—alpha particles, neutrons, protons, deuterons—many transformations have been effected and our knowledge of the constitution of matter has been greatly advanced.

The experiments of the mediæval alchemists, based on vague and ill-defined speculation, ended in failure; the experiments of the modern alchemists, founded on definite and experimentally verified views, have attained a brilliant success. Lead, it is true, has not been changed into gold, but something of much greater importance has been achieved. The modern alchemists, who have pursued their investigations with the sole purpose of increasing knowledge, have, by their discoveries, revealed to us more fully the nature of matter and the structure of the atom; and they have also, as we shall see, opened up visions of great storehouses of energy which may be used to transform the whole material life of man.

The isotopes of elements, now produced in considerable amounts by nuclear transmutation, are becoming increasingly important for certain branches of chemical and medical research because of their use as so-called *tracer elements*. The isotopes of an element although chemically identical, can be distinguished by physical methods; and this is more especially the case when the isotopes are radioactive. They are thereby labelled. If, therefore, a foodstuff, for example, or a compound containing, say, carbon, nitrogen or phosphorus, is prepared from a naturally rare or artificially produced isotope of the ordinary element and is introduced into the body, the track of that compound through the body can be followed. By this means it has been found, for example, that phosphorus introduced in a meal (*e.g.* in the form of sodium phosphate) finds its way into the bones within a few hours. Similarly, by administering an iodide prepared from the radioactive isotope I^{131}, one can readily detect the passage of this element to the thyroid gland; and the circulation of the blood can be followed by means of sodium chloride prepared from radioactive sodium, Na^{24}.

Artificially produced radioactive isotopes, some of which have a comparatively short 'half-life', are of great value not only as tracer elements but also in radiotherapy and for the treatment of disease. Thus, the isotope of cobalt, Co^{60}, which emits gamma rays of similar energy to those of radium, is used as a substitute for that much more expensive element; and Cs^{137} may be similarly used. An artificially prepared radio-isotope of phosphorus, P^{32}, has been used in the treatment of leukæmia and other blood disorders.

Artificially produced radioactive isotopes, owing to the radiations they emit, are also finding important uses in industry for the radiographic examination of metal castings; for the dissipation of static electricity, produced in a number of manufacturing operations, by rendering the air conducting; and for the control of various processes. By the use of the isotope, C^{14}, the distribution of carbon in steel can be studied (Plate 37).

Nuclear Energy.—The particles forming the nucleus of an atom are held together by very powerful forces, and when the nucleus undergoes radioactive transformation great stores of energy are set free. This fact was realized even in the early days of the study of radioactivity (1903), when it was observed that a quantity of radium maintained itself constantly at a temperature above that of its surroundings.

Each disintegration of an atomic nucleus is accompanied by a decrease of mass, which is converted into energy;[1] and so great is the energy produced by the decrease of mass that one ounce of matter transformed entirely into heat energy would, it has been calculated, be sufficient to convert nearly a million tons of water into steam. The energy liberated, therefore, in atomic nuclear reactions is enormous compared with that set free by a corresponding number of atoms in even the most intense chemical reactions, in which only the outer shells of planetary electrons are engaged. The radioactive transformations, however, are uncontrollable by man.

The discovery that the atoms of matter are vast storehouses of potential energy stirred the imagination and gave rise to the belief that in the complex systems of particles constituting the atoms of matter, there must exist great, untapped and formerly unsuspected reservoirs of energy, compared with which the energy of combustion of all our fuel reserves is quite trifling. If one could only gain control of this atomic or nuclear energy, or could control the process of atomic disintegration so as to bring it about at will, then, it was thought, untold stores of energy would be available to carry on the work of the world when the reserves of coal should be exhausted; or which, in the hands of the evilly disposed, would suffice to shatter the globe. Until 1939, however, neither the former hope nor the latter fear appeared to be well founded.

Although the disintegration of atomic nuclei had been effected by Lord Rutherford in 1919, only one out of many thousands of the bombarding particles brought about disintegration of atomic nuclei. From each successful collision, it is true, energy was gained, but the total energy used up in producing the bombarding particles was far greater than the energy released from the relatively few successful collisions. Moreover, unlike the chemical process of combustion, for example, the atomic disintegrations were not self-propagating, for the energy released by one nuclear disintegration did not suffice to bring about the disintegration of the neighbouring nuclei. There seemed to be little hope, therefore, that it would ever be possible to gain useful energy from the atoms by artificial processes of atomic transformation.

---

[1] It was shown by Einstein, as long ago as 1905, that, according to the theory of relativity, there is no essential difference between mass and energy. The relation between mass and energy is given by the expression, $E = mc^2$, where m is the mass in grams and c is the velocity of light (3×10^{10} centimetres per second). Since c is very large, the energy, expressed in ergs (1×10^3 ergs = 0·239 calorie), which is liberated even by a small decrease of mass is very great.

Early in 1939, the outlook was entirely altered. It had just been discovered by OTTO HAHN, in Germany, that uranium nuclei, when bombarded by neutrons, do not behave like the elements previously studied; and the Danish physicists, C. R. FRISCH and LISE MEITNER, showed experimentally that the uranium nuclei undergo 'fission,' or split into two parts of nearly equal mass. Not only was this process accompanied by the liberation of a large amount of energy, but other neutrons were also released which could then bring about the fission of neighbouring uranium nuclei. For the first time, as the result of investigations carried out by physicists in a number of different countries, there seemed to be an experimental basis for the hope that the store of atomic energy might be usefully released; for, once the fission of uranium nuclei had been initiated in a few atoms, the neutrons produced could bring about the fission of other atoms. A chain process, or *chain reaction*, would thus be established which would propagate itself throughout the mass of uranium with the liberation of a large amount of energy. The energy required to start the chain is very small compared with the total energy liberated.

Natural uranium, as extracted from the ore, consists of the two isotopes, uranium–238 and uranium–235, the former being present to the extent of about 99·3 per cent. Although uranium–238 can undergo fission under the action of fast neutrons, slow neutrons can bring about fission only of uranium–235. In natural uranium the chain reaction, referred to above, does not take place because the fast neutrons do not always bring about nuclear fission in uranium–238, and although these neutrons may be slowed down many of the slow neutrons, which could produce fission of uranium–235, are prevented from doing so through absorption by the relatively abundant uranium–238. There is therefore no multiplication of neutrons and the chain reaction does not take place.

In uranium–235, however, slow neutrons can produce nuclear fission with emission of several neutrons, so that with this isotope a chain reaction can be obtained. Uranium–235, in fact, is the only *naturally occurring* substance by means of which atomic or nuclear energy can be obtained on a large scale.

Unfortunately, at the time these most important discoveries were being made, the world was at war; and it was for the purposes of war, for the production of an atomic bomb, that men first sought to utilize this new source of energy. Since only uranium–235 was suitable for this purpose, this isotope had to be separated from the very much more abundant uranium–238. This separation could be effected only by long and tedious physical processes, one method employed being the diffusion, through a porous partition, of the hexafluoride, UF_6, in the gaseous state at a temperature of about 140° F. The hexafluoride of uranium–235 is slightly less dense and in consequence diffuses through a porous septum slightly more rapidly than the hexafluoride of uranium–238. By repeating the diffusion process some thousands of times, uranium–235 can be obtained in a nearly pure state.

Fortunately, it was found that when U^{238} is bombarded by neutrons which have a velocity (and therefore an energy) intermediate between that required to bring about the fission of U^{238} and U^{235}, a new nucleus is produced with a mass number of 239. This loses an electron and passes into the radioactive element *neptunium* (atomic number 93) which, in turn, passes spontaneously, with emission of an electron, into radioactive *plutonium* (atomic number 94), the half-life of which is about 24,000 years. The plutonium so produced can be separated from the uranium by chemical means. This artificial production or 'breeding' of plutonium can be carried out in the nuclear reactor (p. 308), and is a process of the greatest importance because plutonium, like U^{235}, undergoes fission under the action of slow-moving neutrons, and can maintain the chain reaction.[1]

In making an atomic bomb the aim must be to secure that in a mass of uranium–235 (or of plutonium) the chain reaction, made possible by the release of neutrons in the process of nuclear fission, shall run its course in some very minute fraction of a second. In order that this may take place, there must be a certain minimum amount of uranium or plutonium, because if there is less than this, neutrons will escape without bringing about nuclear fission, and the chain reaction will be broken.

---

[1] It may be that in the future thorium will also be brought into use for the production of nuclear energy, because from it one can produce the isotope U^{233} which behaves similarly to U^{235}.

In constructing the bomb, therefore, two masses of uranium–235 (or of plutonium), each sufficiently small to be stable but large enough, when united, to be greater than the critical size, must be brought together with very great rapidity and made to coalesce (by means, say, of an explosive charge), so that spontaneous and instantaneous disintegration occurs with the maximum release of energy.

It is well known that, in 1945, through the co-operative labours of a large number of scientists drawn from different allied countries, the release of the great stores of energy locked up in the atoms of uranium was achieved; and a new epoch in the world's history and in the history of human civilization began. That this achievement, perhaps the greatest achievement of scientific genius of all time, should have to announce itself to the world through the bursting of an atomic bomb over Hiroshima on 6th August, 1945, is one of the tragedies of our time and civilization.

Liberation of energy may take place not only through nuclear fission but also through *nuclear fusion*.

It is believed that at the high temperature of the sun, say, 20,000,000° C., helium atoms are built up from atoms of hydrogen, and in this process there is a decrease in mass and liberation of a very large amount of energy in the form of heat. Thereby the temperature of the sun is maintained. Hydrogen nuclei, however, contain no neutrons and the formation of atoms of helium, with two neutrons in the nucleus, takes place through a cycle of reactions involving carbon atoms, the carbon acting, we may say, as a catalyst. At two points of the cycle, a proton loses a positron and passes into a neutron and so there are furnished the two neutrons necessary to build up the nucleus of the helium atom. This process requires a certain period of time, which is unimportant for the maintenance of the sun's temperature, but fatal for the production of a bomb.

At a very high temperature, however, such as that produced in an atomic bomb, helium may be formed from a mixture of deuterium and tritium. In this way, then, it may be that a hydrogen bomb can be made which is many times more destructive than the ordinary atomic bomb.

For the peaceful uses of nuclear energy, the fission of uranium-235 must be controlled; and this control is effected in what is called an atomic pile or nuclear reactor. As 'fuel,' natural uranium, enriched it may be with uranium-235, may be used. In order to maintain the fission process in this material, it is necessary to slow down the fast neutrons, by means of a 'moderator,' and so allow them to bring about the fission of uranium-235. As moderator, graphite or heavy water may be used.

A nuclear reactor, then, may be constructed of graphite blocks into which the uranium fuel is inserted. The uranium is enclosed in aluminium tubes in which substances to be acted on by neutrons, if desired, are placed and the products of fission are collected. The fast neutrons which escape from the uranium are slowed down by the graphite and bring about fission of the uranium-235. If the reaction goes too fast, it can be slowed down by inserting into the pile, steel rods containing boron or cadmium, which arrest the reaction by absorbing and removing neutrons. The heat produced in the reactor is removed by a suitable gaseous or liquid cooling material.

In the nuclear reactor large numbers of neutrons are produced, and by means of these many radio-isotopes of different elements have been produced. As has already been indicated, these are proving to be of the greatest value for the advance of knowledge and the alleviation of suffering, as well as in industrial operations. By the action of neutrons on deuterium, for example, tritium is formed; and by the action of neutrons and of other bombarding particles on elements of high atomic number, new elements, with atomic numbers 93 to 101, have been produced artificially (p. 8). The production of neptunium and plutonium from uranium-238 has already been noted.

Here we must conclude. Giving a backward look, we see how, out of the mysticism and obscurantism of the earlier alchemistic period, there has grown the science of chemistry, which offers to the mind a clear and well-ordered account of the laws of chemical combination on the basis of the atomic and molecular theories of Dalton and of Avogadro. We see, also, how during the past hundred and fifty years chemists have produced a great array of substances which, in various ways, have proved of benefit to mankind.

Great, however, as have been the services hitherto rendered by chemistry, its power to contribute to man's comfort and well-being and to the general advancement of civilization and of culture is not yet exhausted. The achievements of the past are but an earnest of what will still be accomplished in the future.

In the present chapter, we have seen how, in more recent years, chemists and physicists, in zealous collaboration, have given to us wider and more wonderful philosophic conceptions regarding the universe of matter, and a deeper insight into its nature and constitution. They have opened up for us a new world of knowledge and of power, into which mankind must show itself worthy to enter.

The discoveries and achievements of men of science, so wonderful and so terrifying in their potentialities for good and evil, are a challenge to man's moral greatness; and it is the responsibility of each individual human being, capable of comprehension, to use these discoveries aright in the service and for the welfare of mankind. Great and successful efforts to this end are being made in different countries, and we can look forward, with increasing hope and confidence, to the time when the stores of nuclear energy will be liberated, not with world-shattering violence but as a steadily flowing stream, controlled and directed for the use and benefit of mankind.

One of the most important events in the history of civilization was the inauguration, at Calder Hall, Cumberland, England, on Wednesday, 17 October, 1956, of the first full-scale nuclear power station in the world, by Queen Elizabeth II.

As this must be the last edition of *Chemistry in the Service of Man* which I can hope to prepare I would, in bidding farewell to my readers, express the hope that they have had as much pleasure in reading my book as I have had in writing it. "*If I have written well and to the point in my story, this is what I myself desired; but if meanly and indifferently, this is all I could attain unto. And here shall be the end.*"

INDEX

Accumulator (*see* Cell, storage)
Acetaldehyde, 266
Acetate, amyl, 264
— butyl, 265
— cellulose, 240
— methyl-α-naphthyl, 285
Acetone, 77, 265
— production of, 265, 266
Acetylene, 54, 69
— and ripening of fruit, 70
— from methane, 69
Acid, acetic, 77, 238, 265
— — from acetylene, 266
— — glacial, 266
— acetylsalicylic, 228
— adipic, 242
— ascorbic, 275
— barbituric, 228
— carbolic, 218
— 2:4-dichlorophenoxyacetic, 284
— hydrochloric, 6, 152
— hydrocyanic, 63
— hydrofluoric, 178
— β-indolebutyric, 285
— 2-methyl-4-chlorophenoxyacetic, 284
— muriatic, 152
— β-naphthoxyacetic, 284
— α-naphthylacetic, 285
— nitric, 6, 137
— — from ammonia, 137
— oleic, 120, 121
— palmitic, 120
— paratartaric, 205
— picric, 83
— prussic, 63
— pyroligneous, 77
— pyrosulphuric, 222
— racemic, 205
— salicylic, 228
— stearic, 50
— sulphuric, 6, 115
— — as weed-killer, 136
— — contact process, 117
— — fuming, 117
— — lead chamber process, 116
— tartaric, 205
— terephthalic, 202
Acidity of a solution, 172
Acids, 167
— ionization of, 170
Acrylic nitrile, polymerised, 244
ACTH, 282
Actinium, 291
Activity, optical, 203
— — and vitalism, 211
— — production of, 213
Adrenaline, 278
Adsorption, 187
Aether, 3
Affinity, chemical, 106
Agate, 142
Agent, catalytic, 110
Agriculture, chemistry and, 124
— colloids in, 190
Air, composition of, 21
— constancy of composition, 24
— element, 3
— liquefaction of, 31
— liquid, 31
— pollution of, 48
ALBERTUS MAGNUS, 5, 106
Alchemists, 4
— achievements of, 6
Alchemy, 4
Alcohol, 257
— absolute, 260
— amyl, 259, 264, 265
— — from pentane, 265
— butyl, 122, 259, 264
— denatured, 260
— ethyl, 257, 265
— — from acetaldehyde, 266
— — from acetylene, 261
— — from cellulose, 237
— — from ethylene, 261
— — from methane, 261
— iso-amyl, 264

Alcohol, iso-butyl, 264
— iso-propyl, 260
— methyl, 77, 122
— motor fuel, 59
— production of, 257
— propyl, 264
— solidified, 193
— uses of, 260
— vinyl, 248
Aldrin, 234
Alizarin, 220
— synthesis of, 220
Alkali, 151
Alkalis, 167
— ionization of, 169
Alkathene, 250
Alloprene, 254
Allotropic forms, 75
Alloy, pyrophoric, 44
Alloys, 86
— non-ferrous, 96
— ultra-light, 180
Almonds, oil of bitter, 224
— — imitation, 224
Alpha rays, 291
— — nature of, 293
Aluminium, 178
— alloys, 180
— anodizing, 179
— bronze, 98
— electrical conductivity of, 179
— foil, 179
— isolation of, 178
— reflection of light by, 179
— silicate, 162
— slow combustion of, 40
Alumino-thermic reaction, 42
Alundum, 181
Amatol, 84
Ambergris, 224
Ambrein, 224
Amethocaine, 227
Amethyst, 142
Ammonia, catalytic oxidation of, 137
— from coal, 61
— synthetic, 131
Ammonia-soda process, 151
Ammonium cyanate, 196
— nitrate, 84, 137
— phosphate, 128
— sulphate, 133
— thiocyanate, 63
Amylo-process, 260
Anaesthetics, 227
Analysis, positive ray, 297
Aneurine, 274
Anhydrite, 118, 133
Anions, 170
Anisic aldehyde, 224
Anode, 170
— mud, 176
Anodizing, 179
Anthracene, 218
Anthracite, calorific value of, 45
Anthraquinone, 220
— synthesis of, 221
Antibiotics, 231
Antrycide, 229
Aqua fortis, 6
— regia, 6, 89
Aquamarine, 98
Architecture, molecular, 197
Ardil, 242
Argol, 263
Argon, 26, 27
ARISTOTLE, 3
ARRHENIUS, 169
Arsenious sulphide, colloidal, 186
Arsphenamine, 229
Aspirin, 228
ASTON, 297
Asymmetry, molecular, 208
Atebrine, 230
Atmosphere, gases of the, 21, 25
Atom, electronic constitution of, 290
— structure of, 294
Atomic number, 296
— theory, 9, 11
— weights, 12, 13
Atoms, early views regarding, 10
— mass of, 289
— objective reality of, 287
— relative weights of, 12
Aureomycin, 232
Avlosulfon, 231
AVOGADRO, 11
— law of, 293

Babbitt metals, 101
BACON, 5, 79
BAEKELAND, 247
Bakelite, 247
Baking powders, 152
Barbitone, 228
Barbiturates, 228
Barilla, 151

Bath salts, 152
Bauxite, 178
BECQUEREL, 290
Beers, 261, 263
Beetle ware, 249
Bell metal, 98
Benzaldehyde, 224
Benzene, 217
— formula of, 201
— hexachloride, 234
Benzole, 217
Benzoline (benzine), 54
BERGIUS, 57
BERTHELOT, 269
Beryl, 98
Beryllium, 98
BERZELIUS, 110
Bessemer process, 94
BEVAN, 239
Beverages, alcoholic, 261
BHC, 234
Biochemistry, 269
Biotin, 278
Biscuit ware, 163
Bisque, 163
Blast furnace, 92
Blasting gelatin, 83
Bleaching powder, 153
Blowpipe, 66
— atomic hydrogen, 68
— oxy-acetylene, 70
— oxy-coal-gas, 66
— oxy-hydrogen, 67
Bomb, atom, 306
— hydrogen, 307
Bonds (valency), 16
Bordeaux mixture, 99
Boron and health of plants, 135
Bort, 75
Bouncing putty, 251
BOYLE, 4, 6
Brandy, 262
Brass, 97
— season-cracking of, 98
Brisance, 81
Britannia metal, 101
Bromine, 91
Bronze, 101
— coinage, 98
Bronzes, 98
BROWN, CRUM, 213
BROWN, ROBERT, 194
Brownian movement, 194
— — and molecular magnitudes, 195
B.Th.U., 46
BUCHNER, 256
Buna, 253
— N, 253
— S, 253
BUNSEN, 65
— burner, 65
Butadiene, 253
Butane, 44, 53, 58
Butanol, 264
Butter substitutes, 120
Butvar, 249
Butyrate, amyl, 264
— ethyl, 264

Caesium, radio-isotope, 303
Cairngorm, 142
Calciferol, 276
Calcite, 161
Calcium, bicarbonate, 158
— bisulphite, 237
— carbide, 130
— carbonate, 161
— cyanamide, 130
— hydroxide, 23, 161
— oxide, 161
— phosphate, 127
— sulphate, 118, 133
Calgon, 158
Caliche, 91
Calomel, 100
Calor gas, 58
Calorie, 46
Camphor, 225
Candles, 50
— paraffin, 50
— stearin, 50
— snuffing of, 49, 50
— wax, 50
Carbamate, isopropyl phenyl, 285
Carbohydrates, 236
— synthesis of, 25
Carboloy, 104
Carbon, allotropic forms of, 75
— atom, asymmetric, 209
— — tetrahedral, 208
— black, 78
— chemistry of, 196
— circulation of, in nature, 24
— dioxide, 22
— — and aerated water, 22
— — in expired air, 40

Carbon dioxide, in fire extinguishers, 23
— — preparation of, 22
— — production in fermentation, 265
— — solid (snow), 23
— — test for, 23
— — use in blasting, 24
— disulphide, 63, 239
— isotope, 303
— monoxide, 68
— — flame of, 64
— — from methane, 123
— — oxidation of, 69
Carbonado, 75
Carbonyl chloride, 69
Carborundum, 181
Carboxy-haemoglobin, 69
Carnallite, 126
Carotene, 272
CAROTHERS, 242
CASALE, 133
Casein, 241, 267
Cassiterides, 101
Cassiterite, 101
Catalysis, 105, 110, 112
— in heterogeneous systems, 112
— in industry, 115
— in nature, 114
— negative, 111
— positive, 111
Catalyst, 110
— copper as, 111, 114
— enzymes as, 115
— moisture as, 110
— nickel as, 121
— nicotine as negative, 112
— platinum as, 112, 113, 117
— poisoning of, 113, 118
— tin as negative, 111
Catechol, 279
Cathode, 170, 288
— rays, 288
Cations, 170
CAVENDISH, 25
Celanese, 240
Cell, dry, 102, 173
— Edison, 175
— Leclanché, 102, 173
— storage, lead, 174
— — nickel-cadmium, 175
— — nickel-iron, 175
— voltaic, 165, 172
Cellon, 246
Cellophane, 240
Celluloid, 245
— non-inflammable, 246
Cellulose, 236
— acetate, 246
— alcohol from, 237
— calorific value of, 45
— constitution of, 237
— glucose from, 237
— hydrolysis of, 237
— lacquers, 246
— nitrates, 80, 239
— production in plants, 25
— xylose from, 238
Cement, Portland, 93, 118, 163
Centigrade scale of temperature, 24
Centimetre, 291
— cubic, 26
Cerechlor, 254
Ceria, 71
Cerium-iron alloy, 44
CHADWICK, 301
Chain, branched, 199
— straight, 199
Chalk, 161
Chance in discovery, 113, 231
Charcoal, 77
— activated, 77
— adsorption by, 77, 187
— decolorising liquids by, 78
— use in gas masks, 78
DE CHARDONNET, 238
Cheese, 267
Chemeia, 4
Chemist, meaning of, 2
Chemistry and agriculture, 124
— and electricity, 164
— cultural value of, 2
— definition and scope of, 1
— in space, 208
— medical, 6
— organic, 196
— — synthetic, 215
Chemotherapy, 228
CHEVREUL, 50
Chile saltpetre, 91, 129
China, 162
Chloral, 228
Chloramphenicol, 232
Chlorine, 152
— isotopes of, 297
— production by electrolysis, 176
Chloride of lime, 153

Chloroform, 227
Chloromycetin, 232
Chloroprene, 253
Cholecalciferol, 276
Chromatography, 188
Chromium, 100
— plating, 100
Cinnabar, 100
Classification, periodic, of elements, 17
CLAUDE, 133
Clay, 162
— white china, 162
Coal, 45
— calorific value of, 45
— carbonization of, 48, 60, 61
— complete gasification of, 66
— tar, 217
— utilization of, 47
Coal-gas, 60
— calorific value of, 67
— composition of, 64
— enriching of, 67
— flame, luminosity of, 64
— manufacture of, 61
— purification of, 63
Coalite, 48
Cobalt, 100
— alloys, 100
— as trace element, 283
— in agriculture, 135, 283
— radio-isotope, 303
Cocaine, 227
Coinage, brass, 97
— bronze, 98
— cupro-nickel, 89
— gold, 88
— silver, 89
Coke, 48
Collodion, 82, 246
Colloid particles, size of, 186
Colloids, 183
— emulsoid, 188
— — protective action of, 192
— in soil, 190
— mutual precipitation of, 189
— precipitation of, by electrolytes, 189
— suspensoid, 188
Combustion, 33
— by means of combined oxygen, 42
— explanation of, 34, 35, 41
— in absence of oxygen, 41
— in air, 35
— slow, 39
— — in the living organism, 40
— — of aluminium, 39
— — of iron, 39
— spontaneous, 41
Compound, chemical, 14
Compounds, 8
— optically active, 203, 213
Concentration, influence of, on velocity of reaction, 107
Concrete, 163
Condensation, 237, 245
Condenser tubes, 97, 98, 99
Constitution, atomic, 290, 294
— molecular, 198
— of matter, 2, 290
Copper, 96
— alloys, 98
— as trace element, 283
— cables, 97
— electrolytic, 97, 176
— in agriculture, 136
— refining of, 97, 176
— sulphate, 99
Coral, 161
Cordite, 83
Cortisone, 282
Corundum, 68
Cotton, 236
— mercerised, 241
— nitration of, 80
Coumarin, 224
COUPER, 198
Co-valency, 300
Cracking of oil, 55, 56
Cream of tartar, 263
Cresols, 218
CROOKES, 28, 129, 288
— tube, 288
CROSS, 239
Cryolite, 178
Crystal (glass), 148
Crystallization, velocity of, 141
Crystalloids, 183
Crystals, enantiomorphic, 207
— hemihedral, 205
— holohedral, 205
Cupro-nickel, 89
CURIE, M. S., 290
CURIE, P., 290
Cyanocobalamin, 278
Cyclonite, 84
Cyclotron, 302

2:4-D, 136, 284
Dacron, 244
DALTON, 11
Dapsone, 231
DAVIS, 271
DAVY, 38, 117, 165, 227
DDT, 233
Deacon's process, 152
Decalin, 218
Decolorising liquids by charcoal, 78
Deduction, 20
Deltas, formation of, 189
DEMOCRITUS, 9
Derris root, extract of, 233
Detergents, soapless, 157
Detonators, 81
Deuterium, 298
— oxide, 298
Deuterons, 302
Devitrification, 142
DEWAR, 31
— vacuum vessel, 31
Dextran, 268
Dextrin, 263
Diakon, 250
Dialysis, 184
Di-ammon-phos, 128
Diamond, 75
— arrangement of atoms in, 76
— crystalline structure of, 76
Diastase, 258
Dibutyl phthalate, 235
Dieldrin, 234
Diffusion in solution, 182
Dimethyl phthalate, 235
Dips (candles), 50
Disintegration, atomic, theory of, 292
Dispersators, 193
Dissociation, electrolytic, theory of, 169
Distempers, 268
Distrene, 251
DÖBEREINER, 112
— lamp, 112
Dolomite, 180
Drikold, 24
Drugs, 228
Dry-cleaning agents, 54
Dry ice, 24
Dunnite, 83
Duprene, 253
Duralumin, 180
Dutch metal, 97
DYAR, 152
Dyeing, 189
Dyes, aniline, 217, 219
— coal-tar, 219
— indanthrene, 223
— vat, 223
Dynamics, chemical, 106
Dynamite, 83

Earth (element), 4
— composition of, 9
Earthenware, 163
Ebonite, 252
EHRLICH, 228
EINSTEIN, 304
Electricity and chemistry, 164
— conduction of, by solutions, 167
— discharge of, through gases, 288
— in chemical industry, 176
Electro-chemistry, 164
Electrodes, 168
Electrolysis, 168
— mechanism of, 170
— of copper sulphate, 168
— of sodium chloride, 168, 176
Electrolytes, 167
Electron, mass of, 289
Electrons, 289
— planetary, 298
— — arrangement of, 299
— production of, 289
— sharing of, 300
— transfer of, 299
Electrophoresis, 188
Electroplating, 166
Electro-valency, 300
Element, definition of, 7, 298
Elements, 7, 8
— natural families of, 18
— number of, 296
— of Aristotle, 3
— periodic classification of, 17
— production of, 308
— radioactive, 291
— required by plants, 125, 134
— trace, 135, 283, 303
— transmutation of, 4, 300
Elinvar, 95
Elixir, 5
Emerald, 98
Emery, 68
EMPEDOCLES, 3
Energy, 72

— and matter, 304
— liberation of, by nuclear fission, 306, 308
— — by nuclear fusion, 307
— nuclear, 303
— — utilization of, 308
— of chemical reactions, 73
— potential, 72
Enzymes, 255
— action of, 255, 256, 257
EPICURUS, 9
Epinephrine, 279
Epsom salt, 181
Equation, chemical, 23
Equilibrium, chemical, 108
— — influence of concentration on, 108
— — influence of temperature on, 109
Ergocalciferol, 276
Ergosterol, 276
Erinoid, 247
Ester, 244
Esters, 264
Ethane, 53, 58
Ether, 227
'Ethyl,' 57
Ethylene, 53, 227
Explosives, 78
— disruptive effect of, 81
— high, 81
— low, 81
— taming of, 82, 83

Fahrenheit scale of temperature, 24
FARADAY, 168, 186
Fats, chemical nature of, 50
— hydrolysis of, 153
— saponification of, 154
Felspars, 162
Fermentation, 255
— and enzyme action, 257
— bottom, 259
— explanation of, 256
— top, 259
FERRETTI, 241
Fertilizers, 125
— nitrogenous, 128
— phosphatic, 127
— potash, 126
Fibre-glass, 150
Fibres, artificial, 236
Fire (element), 3
— extinguishing, 23, 37
— production of, 33, 43
Fire-damp, 52
FISCHER, 58
Fission, nuclear, 305
Flame, extinction by wire gauze, 38
— luminosity of, 64
Flash lights, photographic, 180
FLEMING, 231
Flint, 142
FLOREY, 232
Fluon, 250
Fluorescent lighting, 27
Fluorine, 177
— compounds of, 178
Fluoro-hydrogen flame, 178
Foamite firefoam, 23
Food factors, accessory, 271
Formaldehyde (formalin), 84
Formula, 13
— constitutional, 199
— graphic, 16, 199
— structural, 199
Fortisan, 240
FRANKLAND, 16
Freon, 178
FRISCH, 305
Frit, 162
Fructose, 257
Fruit essences, artificial, 264
Fuelite, 48
Fuels, 45
— calorific value of, 45, 67
— gaseous, 59, 67
— liquid, 51
— motor, 59
— smokeless, 48
— solid, 45
Fur, 158
Furfural (furfuraldehyde), 259
Fusel oil, 259, 264
Fusion, nuclear, 307

Galalith, 247
GALVANI, 164
Gammexane, 234
Gardenal, 228
Gas from coal, 60
— marsh, 52
— natural, 52, 59
— — calorific value of, 60
— — composition of, 59
— petrol-air, 54
Gases from cracking of oil, 58

TE OF EDUCATION FO
Dept. of Extension
SERVICE.

Gases, kinetic theory of, 182
— oil refinery, 58
— rare, 25
— — identification of, 27
Gasoline, 54, 55
Gelatin, blasting, 83
— colloidal sol of, 192
Gelignites, 83
Gem stones, artificial, 68
German silver, 98
Germanium, 104
Gin, 262
Glass, 139, 144
— annealing of, 146
— armour plate, 147
— as supercooled liquid, 142
— boro-silicate, 148
— coloured (stained), 148
— composition of, 145, 148
— crystal, 148
— devitrification of, 142
— etching, 178
— for table-ware, 144
— hardened (malleable), 146
— heat-resisting, 148
— patent plate, 146
— pyrex, 148
— quartz, 143
— re-inforced, 147
— sheet, 144
— silvered, 150
— toughened, 146
— transparency of, 149
— triplex, 147
— wool, 150
Glucose, 259
— from cellulose (wood), 237
Glycerine, 50, 155
— production of, by fermentation, 268
— synthesis of, 156
Glyptals, 155
'Gob' fires, 41
Gold, 87
— chloride, 89
— colloidal, 186
— fineness of, 88
— fool's, 92
— plating in vacuo, 88
— potable, 186
— white, 88
Graham, 183
Graphite, 75
— arrangement of atoms in, 75
— artificial, 181
— colloidal, 193
— crystalline structure of, 76
Greek fire, 78
GR.S, 253
Guldberg, 107
Gum, British, 263
Gun-cotton, 80
Gun metal, 98
Gunpowder, 79
Gypsum, 127

Haber, 133
Haematite, 92
Half-life of radioactive substances, 292
Halogens, 177
Hancock, 252
Hawthorn blossom (perfume), 224
Heat of reaction, 74
Helium, 28
— atoms, number in 1 c.c., 293
— from hydrogen, 307
— nuclei and α-rays, 293
— nucleus, 295
Hemming, 152
Herschel, 205
Hexamethylene diamine, 242
von Hohenheim, 6
Hooke, 238
Hopcalite, 69
Hopkins, 271
Hormones, 269, 278
— sex, 282
Humus in soil, 190
Hyatt, 245
Hydrocarbons, 51
— aromatic, 52
— paraffin, 53
— saturated, 52, 53
— unsaturated, 53
Hydrogen, 67
— atom, mass of, 289
— chloride, 152, 177
— flame, atomic, 68
— fluoride, 178
— from methane, 123
— from producer gas, 122
— from water-gas, 122
— ion, 170
— — and acid properties, 170
— — hydrated, 170
— molecule, diameter of, 194
— — mass of, 194

— nucleus, 294
— peroxide, 68
— production of, 166, 177, 265
— sulphide, 55, 63
Hydrogenation of coal, 57
— of coal tar, 58
— of oils, 119
Hydrolysis, 153, 237
Hydrometer, 174
Hydroxide ion, 169
— — and alkali properties, 170
Hydroxyl group, 257
Hypnotics, 227
'Hypo,' photographers', 90
Hypothesis, 19

Iatrochemistry, 6
IBA, 285
Ice cream, protective colloids in, 192
Iceland spar, 161
Ignition point, 37
Illuminants, 45
— gaseous, 59
— liquid, 51
— solid, 49
Incandescent mantles, 71
Indicators, acid-alkali, 171
Indigo, 221
— cultivation of, 221
Indigotin, 221
— synthesis of, 221
Induction, 19
Insect repellents, 235
Insecticides, 233
— in agriculture, 137
Insulin, 281
— composition of, 281
Invar, 95
Invertase, 257
Iodine, 91
— radioactive, 303
— tincture of, 91
Ionization in solutions, 169
Ionone, 224
Ions, 168
— in fused salts, 169
— migration of, 170
Iron, 92
— cast, 94
— galvanised, 96
— magnetic ore, 92
— ores, 92
— pig, 93
— pyrites, 92
— rusting of, 96
— tinned, 96, 101
— wrought, 94
Isomerism, 197
Isomers, ortho-, meta, para-, 202
Isoniazid, 232
Iso-octane, 56
Iso-paraffins, 56
Isoprene, 252
Isotopes, 297
Iso-valerate, amyl, 264

JANSSEN, 28
JAPP, 211
Jellies, water-holding power of, 193
Jeyes' Fluid, 218
JOHNSON, 140
JONSON, 5

Kainite, 126
Kaolin, 162
Kaolinite, 162
KEKULÉ, 198
— theory, 198
Kelp, 91
Kerosine, 54
Kieselguhr, 82
KIPPING, 251
Knocking, 56
Krilium, 134
Krypton, 30
KÜHNE, 256
Kupfernickel, 99

Lacquers, nitrocellulose, 246
— bakelite, 247
Lamp, miner's safety, 38
— sodium vapour, 165
Lampblack, 78
Lanital, 241
Laughing gas, 227
LAVOISIER, 34, 35
Law, Boyle's, 19
— of conservation of mass, 35
— — of matter, 35
— of mass action, 107
— of multiple proportions, 11
— of nature, 19
— periodic, 16, 296
— — anomalies, 296
— scientific, 19
LAWES, 127

Lead, 102
— accumulator, 174
— action of water on, 103
— dioxide, 103
— ethyl, 56
— oxides of, 103
— red, 103
— white, 103
Leather, imitation, 246
LE BEL, 208
LEBLANC, 151
Leclanché cell, 173
LEUCIPPUS, 9
Libbey-Owens process, 145
LIEBIG, 35, 125
Light, polarized, rotation of, 203
— polarization of, 203
Lignite, calorific value of, 45
Lily of the valley (perfume), 224
Lime, 160
— burning of, 161
— chloride of, 153
— in soil, 190
— slaked, 23, 161
— transport in soil, 160
— water, 23, 161
Limestone, 161
— caves, 160
— terraces, 161
Limonite, 92
Liquid, supercooled, 141
— crystallization of, 141
Litharge, 103
Lithopone, 102
Litmus, 172
Litre, 26
LOCKYER, 28
LOWE, 241
Lucite, 249
LUCRETIUS, 10, 226
Lumarith, 246
Luminal, 228
Lunar caustic, 87
Lurgi process, 66
Lyddite, 83
Lysol, 218

M. and B. 693, 230
— 760, 230
McCOLLUM, 271
MACINTOSH, 153
Macromolecule, 236
Magisterium, 5
Magnesia, 181
Magnesite, 181
Magnesium, 180
— carbonate, 181
— from sea-water, 180
— in soil, 134
— oxide of, 181
— sulphate, 181
Malt, 258
— sugar, 257
Maltase, 257
Maltose, 257
Manganese, 96
— and health of plants, 135
— as trace element, 283
— steel, 96
Mantle, incandescent, 71
Marble, 161
Margarine, 120
Marsh gas, 52
Mash, 261
Mashing, 259
Mass action, law of, 107
Mass number, 297
Matches, 43
— safety (Swedish), 44
— strike anywhere, 44
Matter and energy, 304
— colloidal state of, 184
— constitution of, 2
— electronic constitution of, 290
— radiant, 288
— terrestrial, composition of, 9
— transmutability of, 4
Mauve, 219
MAYOW, 21
MCPA, 136, 284
MEITNER, 305
Melinite, 83
Men, 261
MeNA, 285
MENDELÉEFF, 16
Mepacrine, 230
MERCER, 241
Mercuric chloride, 100
— salts, 100
— sulphide, 100
Mercurous chloride, 100
— salts, 100
Mercury, 100
— fulminate, 100
— oxide, 8
Mesothorium-1, 292

— half-life of, 292
Meta, 266
Metaldehyde, 266
Metals, 86
— alkali, isolation of, 165
— and planets, 87
— fusible, 103
— non-ferrous, 96
— sacrificial, 181
Methane, 52, 58
— liquid, transport of, 60
Methanol, 77, 122
Method, scientific, 18
Methoxone, 136, 284
Methyl methacrylate, 249
— orange, 172
— salicylate, 224
MEYER, 16
Micro-organisms, action of, 255
Migen, 261
Milk, curdling of, 192
— protective colloids in, 192
Minium, 103
Mirbane, oil of, 224
Mirrors, glass, 150
Mixture, 14
MOISSAN, 177
Moisture, catalytic action of, 110
Molecule, 11
— definition of, 12
Molecules, mass of, 194
— number of, in 1 c.c., 293
— objective reality of, 194
Molybdenum, 96
— in agriculture, 136
Monazite, 71
Monel metal, 99
Mordant, 190
Mortar, 161
Moth repellent, 218
Motor spirit from coal, 57
— — from water gas, 58
Muntz metal, 97
MURDOCH, 60
Musk, imitation, 224
Must, 263

NAA, 285
Naphthalene, 218
Naphthenes, 51
Natalite, 59
Neon, 30
Neoprene, 253
Neptunium, 8, 306
Neutron, 295, 301
NEWTON, 10
Nichrome, 99
Nickel, 99
— carbonyl, 99
— catalytic action of, 121
— plating, 99
— purification, 99
— silvers, 98
Nicol prism, 203
Nicotinamide, 274
Nitrobenzene, 224
Nitro-cellulose, 82, 239
Nitro-celluloses, 80
Nitro-chalk, 133
Nitrogen, 22
— and oxygen, combination of, 130
— assimilation of, 128
— atmospheric, fixation of, 130
— importance of, in nature, 128
— oxides, from ammonia, 137
Nitro-glycerine, 82
Nitrolim, 130
Nitrous oxide, 227
NOBEL, 82
Non-electrolytes, 167
Novocaine, 227
NoXA, 284
Nucleus, atomic, 294
— — constitution of, 294
— — positive charge on, 294
— — structure of, 295
— — mass of, 297
Number, atomic, 296
Nutrition, 269
Nylon, 242

Ochres, 92
Octane value (number), 56
Octet, 299
Oil, burning, 54
— cracking of, 55, 56
— Diesel engine, 54
— from coal, 57
— from coal tar, 58
— from water gas, 58
— fuel, 55, 57
— — calorific value of, 55
— gas, 54
— illuminating, 57
— lubricating, 55, 57, 59
— of bitter almonds, 224

Oil, of winter green, 224
— paraffin, 54
— shale, 57
— solar, 54
Oils, chemical nature of, 50
— hardening of, 119, 121
— hydrogenation of, 119, 121
Oleum, 117
Opal, 142
Open-hearth process, 94
Orlon, 244
Osglim lamps, 30
OSTWALD, 137
Oxidation, 36
Oxy-acetylene flame, 70
Oxy-coal-gas flame, 66
Oxy-hydrogen flame, 67
Oxygen, 22
— production of, 177
Ozone, 74

PALISSY, 124
Paludrine, 230
Pamaquine, 230
Paper, silver, 101
PARACELSUS, 6
Paradichlorobenzene, 218
Paraffin, 55, 57
— hydrocarbons, 53
Paris green, 233
PARKES, 245
Parthenocarpy, 284
Paste, 148
PASTEUR, 205, 256
Pearls, 161
Peat, calorific value of, 45
— use of, 47
'Pelican,' 5
Penicillin, 231
Pentothal, 227
Peptase, 264
Peptization, 193
Peptones, 264
Perfumes, synthetic, 224
PERKIN, 219
Permutit, 159
PERRIN, 300
Perspex, 249
Pertite, 83
Petrol, 54, 55
— air gas, 54
— by platforming, 56
— from coal, 57
— from coal-tar, 58
— from natural gas, 58
— from oil shale, 57
— from refinery gas, 58
— from water-gas, 58
— lighters, 44
Petroleum, 51
— benzine, 54
— crude, 54
— distillation of, 54
— ether, 54
— fractions, 54
— origin of, 51
— refining of, 55
Pewter, 101
pH, 172
Phenobarbitone, 228
Phenol, 218
Phenolphthalein, 171
PHILLIPS, 117
Philosopher's stone, 5
Phlogiston, theory, 34
Phosphate, calcium, 127
Phosphorus in matches, 44
— isotope, 302
— red, 44
— white, 44
Photography, 90
— by infrared light, 91
— by ultraviolet light, 91
Phthalate, butyl, 265
Pitch, 55
Pitchblende, 290
Plant-growth regulators, 283
Plasmoquine, 230
Plastics, 236, 244
— thermoplastic, 244
— thermosetting, 244
Platinite, 96
Platinum, 91
— as catalyst, 112, 113, 117, 137
PLÜCKER, 288
Plutonium, 8, 306
Polarization of light, 203
Polaroid, 203
Polyesters, 244
Polyethylene (polythene), 250
Polymer petrol, 58
Polymerization, 58, 245
Polystyrene, 251
Polyvinyl chloride, 250
Porcelain, 162
Positron, 295

Potash, caustic, 154
Potassium, 165
— carbonate, 126
— hydroxide, 154
— salts, 126
Potato sprouting, inhibition of, 285
Powder, smokeless, 82
Powders, baking, 152
Power stations, nuclear, 309
PRIESTLEY, 22
Producer gas, 67
Propane, 53, 58
Propylene, 53
Proton, 294
PROUT, 287
Prout's hypothesis, 287
Pulp, sulphite, 237
Purple, Tyrian, 219
Pyrene fire extinguisher, 37
Pyrethrins, 233
Pyrex ware, 148
Pyridoxin, 278

Quartz, 142
— glass, 142
Quicklime, 161
Quinine, 229

Racemates, 206
— resolution of, 206, 210
Radioactivity, 290
— decay of, 292
Radium, 290
— chloride, 290
— disintegration of, 291
— half-life of, 292
— radioactivity of, 291
Radon, 30, 291
— half-life of, 292
RAMSAY, 26, 27, 28, 30, 293
RAYLEIGH, 26, 27
RAYLEIGH (R. J. Strutt), 288
Rayolanda, 240
Rayon, 239
— acetate, 240
— delustred, 239
— staple fibre, 240
Rays, alpha, 291
— — nature of, 293
— beta, 291
— cathode, 289
— gamma, 291
R.D.X., 84
Reaction, chain, 305
— heat of, 74
Reactions, endothermal, 74
— exothermal, 74
— reversible, 108
— velocity of, 105, 106
— — influence of catalysts on, 110
— — influence of concentration on, 107
— — influence of temperature on, 107
Reactor, nuclear, 308
Refraction, double, 161
Rennin, 267
Resins, ion-exchange, 160
— phenol-formaldehyde, 247
— synthetic, 247
— urea-formaldehyde, 249
Riboflavin, 275
Rings, closed, 202
Rock crystal, 142
VON RÖNTGEN, 290
Rooting of cuttings, 285
ROSSITER, 249
Rotenone, 233
Rubber, 251
— hard, 252
— synthetic, 252
Rubber-like materials, 251
Rubies, artificial, 68
Rum, 262
Rupert's drops, 146
Rushlight, 50
RUTHERFORD, D., 22
RUTHERFORD, LORD, 292, 293, 301
Rutile, 68

SABATIER, 121
Safety lamp, 38
Salt, spirit of, 6
Saltpetre, Chile, 91, 129
Salts, 167
Saltwort, 151
Salvarsan, 229
Saponification, 154
Sapphires, artificial, 68
DE SAUSSURE, 24
Scale, boiler, 158
SCHEELE, 22
SCHÖNBEIN, 80
Science, method of, 18
Scurvy, 270
Sea-sand, 142
Season-cracking, 98

Sedimentation in rivers, 189
Seekay wax, 218
SENDERENS, 121
Sewage farms, 191
— purification of, 191
Shale oil, 57
Shimosite, 83
Siemens-Martin process, 94
Signs, illuminated, 27, 30
Silica, 142
— gel, 187
— glass, 142
Silicones, 251
Silk, artificial, 238
— natural, 238
Silver, 89
— bromide, 90
— chloride, 90
— coinage, 89
— German, 98
— iodide, 90
— paper, 101
— sterling, 89
— tarnishing of, 89
Silveroid, 98
SIMPSON, 227
Slag, basic, 95, 128
— blast-furnace, 93
Smoke, production of, 47
Soap, 153
— cleansing power of, 156
— emulsifying action of, 156
— hard, 155
— manufacture of, 154, 155
— soft, 154
— transparent, 155
Soaps, commercial, 155
SOBRERO, 82
Soda, 150
— baking, 152
— caustic, 154, 176
— washing. 152
SODDY, 292
Sodium, 165
— ammonium racemate, 206
— — tartrate, 206
— bicarbonate, 152
— carbonate, 150, 152
— chloride, 14
— — electrolysis of, 168, 176
— cyanide, 165
— hydroxide, 176
— nitrate, 91, 129
— radioactive, 303
— sulphate, 152
— sulphite, 111
— thiosulphate, 90
Sol, colloidal, 184
Solapsone, 231
Solder, plumber's, 101
— tinsmith's, 101
Solid, amorphous, 141, 142
— crystalline, 140
Solute, 182
Solution, 182
Solutions, acid, 172
— alkaline, 172
— electrolytic, 167
— neutral, 172
SOLVAY, 152
Somonal, 228
Soot, 78
Soup can, self-heating, 42
Spectroscope, identification of gases by, 28
Spectrum, 28
Spelter, 102
Spirit, methylated, 260
— of salt, 6
— patent still, 259
— proof, 260
— silent, 259
Spirits, 261
— of wine, 257
STAHL, 34
Stalactite, 160
Stalagmite, 161
Starch, production of, in plants, 25
— saccharification of, 260
State, colloidal, 182
States of matter, 140
Stearin, 50
Steel, 94
— chrome, 95
— galvanizing of, 166
— manganese, 96
— nickel, 95
— stainless, 95
— staybrite, 95
— tempering of, 95
— tool, 96
Stellite, 100
Stereochemistry, 208
— and vitalism, 211
Stereo-isomers, behaviour of, 210, 275, 279, 281

STOKES, 203
Stone, philosopher's, 5
Stoneware, 163
Strass, 148
Streptomycin, 232
Structure, atomic, 294
— molecular, 15, 196
STRUTT, R. J. (Lord Rayleigh), 288
Styrene, 251
Sublimate, corrosive, 100
Sucrose, 257
Sugar, production of, in plants, 25
Sulpha-drugs, 230
— guanidine, 230
— pyridine, 230
— thiazole, 230
Sulphanilamide, 230
Sulphetrone, 231
Sulphones, 231
Sulphur, 118
— dioxide, 118
— — removal from flue gases, 49
— from hydrogen sulphide, 119
— from petroleum, 55
— from sulphur dioxide, 119
— trioxide, 116
Sulphuretted hydrogen, 55, 63
Superphosphate, 127
— triple, 128
Suprarenine, 279
Suramin, 229
Surface tension, 156
Suspensions, sedimentation of, 189
SWAN, 238
Sylvine, 126
Sylvinite, 127
Symbols, 13
Syntheses, microbiological, 268
Synthesis of compounds, 198
— — in plants, 24

Teflon, 250
Temperature of sun, 307
Tempering of steel, 95
TENNANT, 153
Terpineol, 224
Terramycin, 232
Terylene, 243
Tetrafluoroethylene, 250
Tetralin, 218
Theory, 20
— atomic, 9, 11
— disintegration, of radioactivity, 292
— electrolytic dissociation, 169
— kinetic, of gases, 182
— of molecular structure, 199
Therm, 64
Thermit, 42
Thermos flask, 31
Thiamine, 274
Thiouracil, 280
Thiourea, 63, 89, 112
THOMSON, 289, 297
Thoria, 71
Thorium, 291, 306
Thyroxine, 280
Tin, 100
Tin-foil, 101
— grey, 102
— islands, 101
— plague, 102
— plate, 96, 101, 166
— white, 101
Tinstone, 101
Titanium, 103
— oxide, 104
— white, 104
T.N.T., 84
Tocopherol, 278
TODD, 278
Toluene, 218
Toluole, 218
Torpex, 84
Touchpaper, 42
Trace elements, 135, 283
Tracer elements, 303
Transformations, radioactive, 291
Transistors, 104
Transmutation of elements, 301
TRAVERS, 30
Trichloroethylene, 227
Trilene, 227
Trinitrophenol, 83
Trinitrotoluene, 83
Tritium, 298
Tritonal, 84
TROPSCH, 58
Trotyl, 84
Tryparsamide, 229
Tungsten, 104
— carbide, 104
Turkey red, 220
Tyndall phenomenon, 184
Type metal, 103
Tyrian purple, 219, 223

Ultramicroscope, 185
Unit, British Thermal, 46
Uranium-235, 305
— -238, 305
— half-life of, 292
— hexafluoride, 306
— nuclear fission of, 305
— oxide, 291
— radioactivity of, 290
Urea, 134, 196
— as fertilizer, 134
UREY, 298

Vacuum vessel, 31
Valence, 15
Valency, 15, 16
— explanation of, 299
Value, calorific, 45
VAN HELMONT, 124
Vanillin, 224
VAN'T HOFF, 208
Velocity of reactions, 106, 107
Verdigris, 99
Vermilion, 100
Veronal, 228
Vicara, 242
Vimlite, 241
Vinegar, 265
Violet, imitation, 224
Viscose, 239
Vitamin A, 272
— B_1, 273
— B_2 complex, 274
— B_6, 278
— B_{12}, 277
— C, 275
— D, 276
— D_2, 276
— D_3, 276
— E, 278
— H, 278
Vitamins, 269, 271
— as co-enzymes, 272
Vitriol, oil of, 115
Volt, 164
VOLTA, 164
Vulcanite, 252

WAAGE, 107
Wash, 259
Water, desalting of, 160
— element, 4
— hard, 158
— — softening of, 158
— heavy, 298
— potable, from sea-water, 160
— removal of salts from, 159
Water-gas, 67
— calorific value of, 67
— carburetted, 67
— semi, 67
— syntheses from, 121
Water-glass, 143
Weedkillers, selective, 136, 284
Weight, atomic, 12, 13
— molecular, 14
Whisky, 261
Windolite, 241
Wine, spirits of, 257
Wines, 261, 262
— bouquet of, 263
— diseases of, 263
— souring of, 265
Wintergreen, oil of, 224
WINZER (WINSOR), 60
Wire-gauze, cooling action of, 38
Woad, 221
WÖHLER, 196
Wood, calorific value of, 45
— distillation of, 77
— glucose from, 237
— spirit, 77
Wort, 259

X-rays, 290
Xenon, 30
Xylenes, 202
Xylonite, 245
Xylose, 238

Yeast, 256, 257
— Chinese, 261

Zakatalsk nuts, 275
Zeolite, 159
Zinc, 102
— as trace element, 283
— blende, 102
— oxide, 102
— sulphide, 102
— white, 102
Zirconium, 181
Zymase, 256, 257

CHEMISTRY
IN THE SERVICE OF MAN

EIGHTH EDITION

by

ALEXANDER FINDLAY

Past President
of the Royal Institute of Chemistry

SINCE the last edition was published in 1947 spectacular advances have been made in chemistry. These have followed the revolution in physics which began with the splitting of the atom, and the final chapter of the book gives a review of these changes. It deals with the constitution of matter, leading up to the peaceful uses of nuclear energy.

The revision is complete. The illustrations are up to date and the book has been reset. Professor Findlay deals with the new drugs, penicillin, and the antibiotics, he gives some account of plastics, nylon, terylene, insecticides, vitamins and hormones. There is also a discussion of radio-active isotopes.

Professor Findlay in his preface tells us that the book is intended for those who need or desire to understand something of the intellectual progress of recent years and to gain some knowledge of a branch of science on which much of our present day civilization is based.

This is one of the few books written by a well-known scientist which the non-scientist can readily understand, and trust.

1724

LONGMANS